Functional Polymers. XLIII. Olefin Copolymers of 2, 6-Di-t-butyl-4-vinyl (or 4-isopropenyl) phenol

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Functional Polymers. XLIII.* Olefin Copolymers of 2,6-Di-t-butyl-4-vinyl (or 4-isopropenyl) phenol

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ABSTRACT

Several new polymeric antioxidants have been synthesized based on 2,6-di-t-butyl-4-vinyl (or isopropenyl) phenol. They were prepared by emulsion copolymerization with 1,3-butadiene or isoprene and had about 6 to 10 mol% of the polymerizable hindered vinyl (or isopropenyl) phenol in the copolymers. The copolymers were catalytically hydrogenated in the presence of soluble cobalt catalysts to saturated copolymers of ethylene or ethylene/propylene structure. The polymers are apparently not branched and had molecular weights up to 50 000.

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INTRODUCTION

Polymer-attached stabilizers have become of increasing interest for polymeric materials which require higher fabrication temperatures and requirements of extended lifetime of the polymers [1, 2]. Not only have polymers with the antioxidant type of functional groups [3] been studied, but also others that have groups that can function as photo-stabilizers and flame retardants [4-8].

Our work has concentrated on the development of efficient methods for the synthesis of 2,6-di-t-butyl-4-vinyl (or isopropenyl) phenol; this has been accomplished [9] and developed into an easy laboratory synthesis [10]. The two compounds, styrene or α-methylstyrene derivatives of highly hindered phenols (as resonance-stabilized monomers), were shown to copolymerize readily with such monomers as styrene, methyl methacrylate, and methyl acrylate [11]. Polymeric stabilizers have also shown effectiveness for the prevention of long-term oxidation of olefin polymers [12]. 2,6-Di-t-butyl-4-vinylphenol in small amounts has been incorporated into 1,3-butadiene copolymers prepared by emulsion polymerization [13].

It was the objective of this work to develop a technique to copolymerize 2,6-di-t-butyl-4-vinyl (or isopropenyl) phenol by emulsion polymerization with 1,3-butadiene or isoprene. Such copolymers were expected to be effective antioxidants for diene polymers. Catalytic hydrogenation was expected to give copolymers containing polymer-bound antioxidant which would be compatible with polyethylene, polypropylene, and ethylene/propylene copolymers. We were aiming for copolymers with from 5 to 10 mol% of 2,6-di-t-butyl-4-vinyl (or isopropenyl) phenol in the diene copolymers.

EXPERIMENTAL

Materials

2,6-Di-t-butyl-4-vinylphenol and 2,6-di-t-butyl-4-isopropenylphenol were synthesized in our laboratory [9, 11]. 1,3-Butadiene (Linde Division, Union Carbide Corporation) was freed from carbon dioxide, and isoprene (Aldrich Chemical Company) was distilled and stored under argon. Triethylaluminum (Ethyl Corporation), cobalt 2-ethylhexanoate (Pfaltz and Bauer, Inc.), 4,4'-azobis(4-cyanovaleric acid) (ACVA) (Aldrich Chemical Company), and argon gas (Linde Division, Union Carbide Corporation) were used as received. Cyclohexane was heated under reflux over calcium hydride, distilled, and stored under argon.

Measurements

Infrared spectra were measured on a Perkin-Elmer Model 283 spectrophotometer. Polymer 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. ^{13}C NMR spectra were recorded 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$_6$. Polymer samples required at least 20 000 transients.

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

Gel permeation chromatography was performed on a Waters Associates Model 201 liquid chromatograph using tetrahydrofuran as solvent.

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

Copolymerization and Hydrogenation

Copolymerization of 2,6-Di-t-butyl-4-vinylphenol with 1,3-Butadiene in Emulsion.

1,3-Butadiene was condensed into a 360-mL polymerization tube until the correct net weight (40.0 g, 740 mmol) had been reached. The tube was then capped with a septum, and the liquid 1,3-butadiene was transferred via a double-tipped needle (under slight pressure of oxygen-free argon) to a 100-mL round-bottom flask, also capped with a septum. containing 2,6-di-t-butyl-4-vinylphenol (100.0 g, 43 mmol, ~6 mol%). The solution was kept below the boiling point of 1,3-butadiene (-4°C), deoxygenated by bubbling oxygen-free argon through it for 30 min, and transferring it via a double-tipped needle to a second 360-mL polymerization tube containing the remainder of the emulsion recipe: ACVA initiator (1.2 g), sodium dodecylsulfate emulsifier (2.5 g), and distilled water (90 mL). This tube had been fitted with a high-vacuum, three-way stopcock; it was kept in a salt/ice bath at -5°C (-5°C is cold enough to maintain 1,3-butadiene below its boiling point as it is being added to the emulsion mixture, but at this temperature the aqueous mixture will not freeze readily). Immediately after the transfer was complete, the tube containing the liquid aqueous phase was rapidly and vigorously shaken to emulsify the contents and then frozen in liquid nitrogen while emulsified.

(Freezing in a nonemulsified aqueous phase will cause expansion which could shatter the polymerization tube.) The time between completion of the comonomer transfer and the freezing was about 1 min. The polymerization tube was evacuated and sealed at 0.01 torr; the contents were thawed slowly, placed in a 65°C water bath, and shaken to keep the contents of the tube emulsified. After 1 week the tube, now containing a light-yellow, stable latex, was removed from the water bath, chilled in ice, and carefully opened. An aqueous lithium chloride solution (10 mL, 10%) was added to the tube with shaking, followed by concentrated hydrochloric acid (5 mL). The mixture was finally added slowly with stirring to 700 mL of methanol; large white clumps of polymer soon coalesced. After allowing the polymer to settle overnight, the supernatant liquid was decanted. The polymer was transferred to a 100-mL beaker where it was dissolved in cyclohexane at room temperature and reprecipitated into 500 mL of methanol. The material was isolated and dried in a vacuum desiccator at 0.1 torr for 1 day. The yield of transparent, slightly amber polymer was 10.6 g (21%). The molecular weight values of the polymer, obtained by gel permeation chromatography (polystyrene standard), were $\overline{M}_n$ = 16 300 and $\overline{M}_w$ = 45 000. Infrared analysis (film) showed bands at 3 650 cm^{-1} (hindered phenol O–H stretch), 1 640 and 1 670 cm^{-1} (cis and trans C=C stretch), and 1 596 cm^{-1} (aromatic C=C stretch). The ^{13}C NMR spectrum (CDCl$_3$) showed peaks at: 30.55 ppm (t-butyl $\underline{C}H_3$); 27.49, 30.18, 32.77, 34.09, 38.22, and 43.57 ppm (butadiene $-\underline{C}H_2-$); 114.21, 128.41, 129.51, 129.66, 130.08, 131.30, and 142.76 ppm (=CH– of polybutadiene with random cis-trans geometry). ^{1}H NMR analysis (CDCl$_3$) showed peaks at δ: 1.4 ppm ($-C(\underline{C}H_3)_3$); 2.0 ppm ($-\underline{C}H_2-$ of polybutadiene); 5.3 ppm (=$\underline{C}H-$ of 1,4-butadiene units); 4.9 ppm ($-\underline{C}H=\underline{C}H_2$ of 1,2-butadiene units); and 6.7 ppm (aromatic). A comparison of integrated areas of the peaks at δ 1.4 ppm ($-C(\underline{C}H_3)_3$) and 4.6–5.6 ppm (=CH–) indicated a copolymer composition of 6% 2,6-di-t-butyl-4-vinylphenol and 94% 1,3-butadiene.

Analysis: Calculated for $-(C_{16}H_{24}O)_{0.06}-(C_4H_6)_{0.94}$: C, 88.45; H, 11.13%. Found: C, 88.24; H, 11.14%.

Copolymerization of 2,5-Di-t-butyl-4-vinylphenol with Isoprene in Emulsion. Freshly distilled isoprene (4.8 g, 70 mmol) was placed in a 50-mL pear-shaped flask containing 2,6-di-t-butyl-4-vinylphenol (0.2 g, 0.9 mmol, 1 mol%); the solution was transferred under argon via a double-tipped needle to a polymerization tube containing the rest of the emulsion recipe: ACVA initiator (0.06 g), sodium dodecylsulfate emulsifier (0.25 g), and distilled water (9 mL). After the emulsion was made, the tube was sealed at 0.1 torr, shaken in a 65°C water bath for 3 days, then opened and the latex coagulated by pouring it with stirring into 250 mL of meth-

anol. The white suspension coagulated into a white clump of polymer; the product was dissolved in cyclohexane and reprecipitated into methanol, dried at 60°C and 0.1 torr for one day to yield 1.13 g (23%) of clear, rubbery polymer. Molecular weights of the material were $\overline{M}_n$ = 23 500 and $\overline{M}_w$ = 121 000. The infrared spectrum (film) showed absorbances at 3 650 cm^{-1} (hindered phenol O–H stretch), 1 640 cm^{-1} (trisubstituted C=C stretch), and 1 507 cm^{-1} (aromatic C=C stretch). The bands at 3 650 and 1 597 cm^{-1} were weak. ^{13}C NMR analysis (CDCl$_3$) showed peaks at 16-40 ppm (alkane resonances of polyiso-

prene) and 110-135 ppm (alkane resonances of polyisoprene). The ^{1}H NMR spectrum showed peaks at δ: 1.4 ppm ($-$C(C$\underline{\text{H}}_3$)$_3$); 1.6 and

1.7 ppm ($-$C$\underline{\text{H}}_3$ of cis, trans polyisoprene); 2.0 and 2.1 ppm ($-$C$\underline{\text{H}}_2-$ of polyisoprene); 4.6 and 5.0 ppm (=C$\underline{\text{H}}_2$ of 3,4 and =C$\underline{\text{H}}-$ of 1,4 isoprene units, respectively).

Analysis: Calculated for $+$C$_{16}$H$_{24}$O$\rightarrow_{0.08}$$+C_5H_8\rightarrow_{0.92}$: C, 87.72; H, 11.71%. Found: C, 87.42; H, 11.32%.

Copolymerization of 2,6-Di-t-butyl-4-vinylphenol with Isoprene in Bulk. A polymerization tube was charged with 2,6-di-t-butyl-4-vinylphenol (0.4 g, 1.7 mmol, 1 mol%) dissolved in freshly distilled isoprene (9.6 g, 140 mmol) and ACVA (0.23 g, 1.7 mmol, 1 mol%). The tube was degassed by the freeze-thaw technique, sealed at 0.01 torr, and placed in a 65°C water bath. After 5 days the polymer was isolated by pouring the contents of the tube into 500 mL of stirred methanol. The precipitate was isolated, dried at 60°C and 0.1 torr for 1 day to yield 2.06 g (21%) of a viscous liquid. Molecular weights of the polymer were $\overline{M}_n$ = 6 300 and $\overline{M}_w$ = 9 000, determined

by gel permeation chromatography. The infrared spectrum showed absorption peaks at 3 650 cm^{-1} (hindered phenol O–H stretch), 1 665 cm^{-1} (trisubstituted C=C stretch), and 1 640 cm^{-1} (vinylidene C=C stretch from 3,4 addition).

Analysis: Calculated for $+$C$_{16}$H$_{24}$O$\rightarrow_{0.01}$$+C_5H_8\rightarrow_{0.99}$: C, 88.10; H, 11.82%. Found: C, 88.01; H, 11.82%.

Copolymerization of 2,6-Di-t-butyl-4-isopropenylphenol with 1,3-Butadiene in Emulsion. 1,3-Butadiene (40.0 g, 740 mmol) was condensed into a 360-mL polymerization tube and transferred under pressure of oxygen-free argon to a 100-mL round-bottom flask containing 2,6-di-t-butyl-4-isopropenylphenol (10.0 g, 41 mmol, ~6 mol%). The solution was transferred via a double-tipped needle to a 360-mL polymerization tube containing the remainder of the emulsion recipe: ACVA initiator (1.2 g), sodium dodecylsulfate emulsifier (2.5 g), and distilled water (90 mL). The tube was shaken rapidly and vigorously to emulsify its contents, sealed at 0.01 torr, placed in a 65°C water bath, and shaken for 1 week; a light-yellow, stable latex formed. Aqueous lithium

chloride solution (10°C, 10 mL) and 5 mL of concentrated hydrochloric acid were added, and the coagulated latex was added slowly to 700 mL of rapidly stirred methanol. The precipitate, white clumps of polymer, was isolated, redissolved in cyclohexane, and reprecipitated into 500 mL of methanol. A gelatinous product was obtained and dried at 0.1 torr for 24 h. The yield of clear, light-amber, sticky polymer was 7.9 g (16%). The molecular weights for the polymer, obtained by gel permeation chromatography, were $\overline{M}_n$ = 13 000 and $\overline{M}_w$ = 25 700.

Infrared analysis (film) showed bands at 3 650 cm^{-1} (hindered phenol O–H stretch), 1 640 and 1 670 cm^{-1} (cis and trans C=C stretch), and 1 596 cm^{-1} (aromatic C=C stretch). The ^{13}C NMR spectrum (CDCl$_3$) showed peaks at: 30.22 ppm (–C($\underline{C}$H$_3$)$_3$); 27.49; 30.18, 32.77, 34.09, 38.22, and 43.57 ppm (–$\underline{C}$H$_2$– of random cis, trans-polybutadiene); and 114.21, 128.41, 129.51, 129.66, 130.08, 130.51, 131.30, and 142.76 ppm (=$\underline{C}$H– of random cis, trans-polybutadiene). ^{1}H NMR analysis (CDCl$_3$) showed peaks at δ: 1.4 ppm (–C($\underline{C}$H$_3$)$_3$); 2.0 ppm (–$\underline{C}$H$_2$– of polybutadiene); 5.3 ppm (=$\underline{C}$H– of 1,4-butadiene unit); 4.9 ppm (–$\underline{C}$H=CH$_2$ of 1,2 unit); and 6.7 ppm (aromatic). A comparison of integrated areas of the peaks at 1.4 and 4.9-5.3 ppm indicated a copolymer composition of 6% 2,6-di-t-butyl-4-isopropenylphenol and 94% butadiene.

Analysis: Calculated for $\{C_{17}H_{26}O\}_{0.06}\{C_4H_6\}_{0.94}$: C, 88.46; H, 11.15%. Found: C, 88.21; H, 11.03%.

Copolymerization of 2,6-Di-t-butyl-4-isopropenylphenol with Isoprene in Emulsion. In freshly distilled isoprene (35.8 g, 525 mmol) was dissolved 2,6-di-t-butyl-4-isopropenylphenol (6.5 g, 26 mmol, 5 mol%); at 0°C the solution was transferred to a polymerization tube containing the rest of the emulsion recipe: ACVA initiator (1.2 g), sodium dodecylsulfate emulsifier (2.5 g), and distilled water (90 mL). The tube was shaken to emulsify the contents and sealed at 0.01 torr. After 1 week at 65°C the tube was opened and the latex coagulated by addition of 10% aqueous lithium chloride solution (10 mL) and concentrated hydrochloric acid (5 mL), and the mixture poured into 700 mL of stirred methanol. After isolating the white polymer, it was dissolved in cyclohexane and reprecipitated into methanol. The polymer was dried at 0.1 torr in a vacuum desiccator. Yield of clear rubbery polymer was 7.4 g (18%). Molecular weights of the material, as determined by gel permeation chromatography, were $\overline{M}_n$ = 10 500 and $\overline{M}_w$ = 18 500. The infrared spectrum (film) showed absorbances at 3 650 cm^{-1} (trisubstituted C=C stretch) and 1 597 cm^{-1} (aromatic C=C stretch). ^{13}C NMR analysis (CDCl$_3$) showed peaks at 16-40 ppm (alkane resonances of polyisoprene) and 110-135 ppm (alkene resonances of polyisoprene). The peak at 30.2 ppm, due to –$\underline{C}$H$_3$ of the tertiary butyl group of the phenolic monomer,

was covered by isoprene peaks. ^{1}H NMR $(CDCl_3)$ showed peaks at δ: 1.4 ppm $(-C(CH_3)_3)$; 1.6 and 1.7 ppm $(-CH_3$ of cis, trans-polyiso-prene); 2.0 and 2.1 ppm $(-CH_2-$ of polyisoprene); 4.6 and 5.0 ppm $(=CH_2$ of 3,4- and $=CH-$ of 1,4-isoprene units, respectively). Comparison of integration areas for the peaks at 1.6-1.7 and 1.4 ppm indicated a copolymer composition of 4% 2,6-di-t-butyl-4-isopropenyl-phenol and 96% isoprene.

Analysis: Calculated for $-(C_{17}H_{26}O-)_{0.06}-(C_5H_8-)_{0.94}$: C, 87.84; H, 11.75%. Found: C, 86.71; H, 11.61%.

Catalytic Hydrogenation of Copolymers of 2,6-Di-t-butyl-4-vinylphenol or 2,6-Di-t-butyl-4-iso-propenylphenol with 1,3-Butadiene or Isoprene. Poly(2,6-di-t-butyl-4-vinylphenol-co-1,3-butadiene) (2.2 g, 40 mmol of unsaturation, 6 mol% phenolic units) was placed in a 100-mL round-bottom flask. The flask was capped with a septum, flushed with oxygen-free argon, and charged with dry cyclohexane (100 mL). After the polymer had dissolved, the cyclohexane solution was transferred via a double-tipped needle to an assembled 160-mL stirred and thermo-statted reactor. Next, triethylaluminum/cobalt 2-ethylhexanoate catalyst (0.67 mL of a 0.178 M solution in cyclohexane, 7 mol%) was added to the reactor by syringe and charged to 300 psi five times, venting each time. Finally, the reactor was pressurized with hydro-gen to 50 psi and heated to 50°C. After 1 h the stirred reactor was cooled, vented, and opened. The black solution was shaken vigorously with 10% hydrochloric acid (30 mL) until it turned pink, signifying formation of the aquo cobalt complex. The emulsion was added to 500 mL of stirred methanol to precipitate the polymer. The off-white product was collected on a sintered-glass funnel and purified by dis-solution in cyclohexane and reprecipitation into methanol. The poly-mer was dried at 60°C and 0.1 torr for 12 h. Yield of white, spongy solid was 0.3 g (60%). Infrared analysis (film) showed peaks at 3 650 cm^{-1} (hindered phenol O–H stretch), 2 930-2 860 cm^{-1} (alkane C–H stretch), 1 465-1 450 cm^{-1} (CH_2 and CH_3 deformation), and 720 cm^{-1} (alkane C–H rocking). ^{13}C NMR (benzene-d_6) showed a major peak at 30.2 ppm $(-CH_2-)$ and minor peaks at 27.44, 30.71, and 34.02 ppm (alkane branches). ^{1}H NMR (benzene-d_6) showed one peak at 1.4 ppm (broad; alkane protons).

Analysis: Calculated for $-(C_{16}H_{24}O-)_{0.06}-(C_4H_8-)_{0.94}$: C, 85.45; H, 14.13%. Found: C, 83.78; H, 13.76; ash, 2.1%.

The procedure for hydrogenation of poly(2,6-di-t-butyl-4-isopro-penylphenol-co-1,3-butadiene) was identical to that described above; the spectral and physical properties of the polymer obtained were similar.
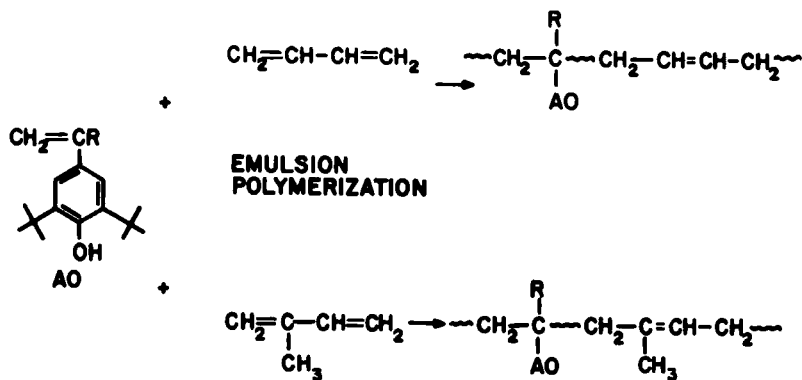
Copolymers of 2,6-di-t-butyl-4-vinylphenol and 2,6-di-t-butyl-4-isopropenylphenol with isoprene were hydrogenated in a similar manner using 10 mol% triethylaluminum/cobalt 2-ethylhexanoate catalyst. After precipitation and drying, the brownish polymer was tough and rubbery. Infrared analysis (film) of the hydrogenated isoprene copolymers showed peaks at: 3 650 cm^{-1} (hindered phenol O–H stretch), 2 980-2 850 cm^{-1} (alkane C–H stretch), 1 470-1 450 cm^{-1} (CH$_2$ and CH$_3$ deformation), and 732 cm^{-1} (alkane C–H rocking). ^{13}C NMR analysis (benzene-d$_6$) showed peaks at: 20.08, 25.08, 28.05, 33.37, 33.71, 35.01, and 38.06 ppm (branched and linear alkane absorptions). ^{1}H NMR analysis showed only two broad peaks, one at 1.0 ppm (–CH$_3$) and one at 1.3 (–CH$_2$–).

Analysis: Calculated for $-(C_{17}H_{26}O-)_{0.06}-(C_5H_{10}-)_{0.94}$: C, 85.46; H, 14.15%. Found: C, 84.24; H, 14.65; ash, 2.2%.

RESULTS AND DISCUSSION

Two polymerizable derivatives of 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-vinyl (or 4-isopropenyl) phenol, have been copolymerized with 1,3-butadiene and isoprene, and the backbone unsaturation which remained from the butadiene and isoprene units was hydrogenated to units of "ethylene"or "ethylene/propylene alternating copolymer."

2,6-Di-t-butyl-4-vinylphenol and O-acetyl[4-vinyl]2,6-di-t-butyl-phenol were synthesized in overall yields of about 50 and 80%, respectively, starting from 2,6-di-t-butylphenol. 2,6-Di-t-butyl-4-isopropenylphenol was also obtained in about 50% yield. 2,6-Di-t-butyl-4-vinyl (or 4-isopropenyl) phenol were copolymerized by radical emulsion polymerization using ACVA as the generator of the initiating radicals:

   Polymerization of the free-phenol monomers 2,6-di-t-butyl-4-
vinyl (or 4-isopropenyl) phenol was not straightforward. Trace
amounts of oxygen in the medium provided macroperoxy radicals
whose growth can be inhibited by the phenolic –OH group of the anti-
oxidant. Numerous methods of removing oxygen from the polymeriza-
tion medium were explored, including freeze-thaw cycles and evacua-
tions, but it affected adversely the emulsion stability. The best results
were obtained when specially purified inert gas (e.g., argon) was used
and the emulsion carefully purged.
   A similar amount of effort went into the choice of initiator for
the emulsion copolymerization of free-phenol monomers. Use of
potassium persulfate, a common radical initiator, led to oxygen-
type radicals and very low yields of polymers. Although ACVA will
dissolve to only a few weight percent in water, copolymer yields of
up to 25% were obtained with ACVA as the initiator for the emulsion
polymerization.
   In the copolymerization of 2,6-di-t-butyl-4-vinylphenol with 1,3-
butadiene, several further problems were encountered. First, the
volatility of butadiene (bp = -4°C) made it essential that all manipu-
lations of this material be done below this temperature. Also, con-
siderable pressure (50-60 psi) was built up in the initial part of the
polymerization inside the tube which was used for the polymeriza-
tion. For this reason, glass tubes with medium-thick walls (3.2 mm
or more) were used to retain a margin of safety against failure of
the tube. Annealing of the seal also had to be done carefully to pre-
vent failure.
   The method of choice for emulsion polymerization of dienes used
in our laboratory is a modification of Kolthoff's procedure [14]. The
mercaptan molecular weight modifier was omitted since degradative
chain transfer to phenolic monomer occurred to some small extent
which modified the molecular weight.
   A safe anaerobic technique could also be used for incorporating
low levels of hindered phenolic monomers into emulsion 1,3-buta-
diene copolymers. It helped to preboil the emulsifier solution to
free the solution from oxygen. This method does not affect emul-
sion stability.
   The emulsion recipe, minus the monomers, was made up, placed
in a polymerization tube, and deoxygenated. The solution of mono-
mers was deoxygenated separately, then added to the tube containing
the aqueous mixture, which had been cooled to -5°C. In order to
evacuate and seal the tube, the contents were frozen in liquid nitro-
gen. At this point the reaction mixture had to be thoroughly emulsi-
fied, otherwise expansion could occur which was capable of shatter-
ing the polymerization tube. After opening the polymerization tube
at the end of the reaction (with extreme caution because of the pres-
sure buildup) and after coagulating the latex and precipitating the
product in methanol, the product, a gelatinous mass, was dissolved
in cyclohexane, reprecipitated into methanol, and dried at 0.1 torr.

Yield of the polymer was 21%; the molecular weight analysis by gel permeation chromatography showed $\overline{M}_n$ = 16 300 and $\overline{M}_w$ = 45 000.

The infrared spectrum was consistent with a copolymer of 1,3-butadiene and 2,6-di-t-butyl-4-vinylphenol; the ^{13}C NMR and ^{1}H NMR spectra showed that the butadiene units in the copolymer had a random cis, trans geometry and 1,2 structure by comparison with a copolymer sample of 1,3-butadiene/styrene.

The ^{1}H NMR spectrum further revealed that the 1,3-butadiene units had over 90% 1,4-structure. Integration of the appropriate peaks in the ^{1}H NMR spectrum gave a copolymer composition of 6% phenol and 94% butadiene units, which was borne out by elemental analysis.

No spectral evidence of incorporation of hindered-phenol monomer into the polymer chain through the oxygen atom was seen. This is in line with the small rate constants for reinitiation by hindered phenoxyls [15].

In the emulsion copolymerization of 2,6-di-t-butyl-4-vinylphenol with isoprene, a similar procedure of separate deoxygenation of the monomer mixture and the emulsion matrix was carried out. Isoprene, a liquid with a bp = 35°C, was handled with greater ease. A 23% yield of copolymer was obtained having $\overline{M}_n$ = 23 500 and $\overline{M}_w$ = 121 000 by GPC.

As in the case of the 1,3-butadiene copolymer, the hindered phenol units were clearly identified in the infrared spectrum. Elemental analysis pointed to a copolymer composition of 8% hindered phenol and 92% isoprene.

2,6-Di-t-butyl-4-vinylphenol was also copolymerized with isoprene in bulk, using AIBN as the initiator. The copolymer produced was a viscous liquid with $\overline{M}_n$ of 6 300 and $\overline{M}_w$ of 9 000 by GPC. Even at 1% incorporation of the antioxidant monomer, the hindered phenol peak was still clearly visible at 3 650 cm^{-1} in the IR spectrum.

Copolymerization of 2,6-di-t-butyl-4-isopropenylphenol with 1,3-butadiene or isoprene was carried out using the same procedure as for the vinyl monomer. The 1,3-butadiene copolymer, containing 6 mol% phenolic monomer, according to both ^{1}H NMR spectroscopy and elemental analysis, had $\overline{M}_n$ = 13 000 and $\overline{M}_w$ = 25 700 (by GPC); the yield was 16% of copolymer.

Isoprene copolymerization gave similar results. The yield of poly-(2,6-di-t-butyl-4-isopropenylphenol-co-isoprene) was 18%. $\overline{M}_n$ and $\overline{M}_w$ determined by GPC were 10 500 and 18 500, respectively.

Table 1 summarizes data from several diene polymerizations with 4-vinyl (or 4-isopropenyl) 2,6-di-t-butylphenol. Even under our best reaction conditions, if 10% phenolic monomer was present in the comonomer feed, polymerization was substantially inhibited and the final copolymer was only an oligomer.

TABLE 1. Summary of Molecular Weight Data for Copolymers of Hindered Phenol Monomers and Dienes in Emulsion[a]

Hindered phenol monomer	Amount		Comonomer	Amount		Yield, %	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
	g	mmol		g	mmol				
A. 2,6-Di-t-butyl-4-vinylphenol	0.2	0.9	Isoprene	4.8	70.0	23	23 500	121 000	5.2
B. 2,6-Di-t-butyl-4-vinylphenol	13.6	59.0	Isoprene	36.4	534	~1	3 500	5 000	1.4
C. 2,6-Di-t-butyl-4-vinylphenol	10.0	43.0	Butadiene	40.0	740	21	16 300	45 000	2.8
D. 2,6-Di-t-butyl-4-isopropenylphenol	6.5	26.0	Isoprene	35.8	525	18	10 500	18 500	1.8
E. 2,6-Di-t-butyl-4-isopropenylphenol	10.0	41.0	Butadiene	40.0	740	16	13 000	25 700	2.0

[a]The temperature was 65°C in all cases; the initiator was ACVA. The reaction time was 7 days in all cases except A, when it was 72 h.

Catalytic Hydrogenation of Copolymers of 2,6-
Di-t-butyl-4-vinylphenol or 2,6-Di-t-butyl-4-iso-
propenylphenol with 1,3-Butadiene or Isoprene. The
hydrogenation of copolymers of 2,6-di-t-butyl-4-vinylphenol and 2,6-
di-t-butyl-4-isopropenylphenol with 1,3-butadiene or isoprene was
accomplished using an aluminum/cobalt homogeneous catalyst system
developed by Falk [16-18]. These catalysts rapidly and selectively
hydrogenated polymer backbone unsaturation under mild reaction con-
ditions, while aromatic unsaturation was unaffected [16]:
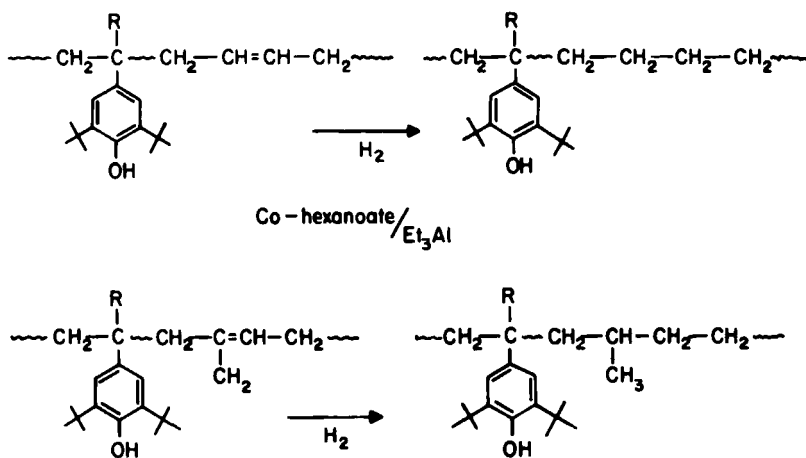
The catalyst system used in this work was prepared by slow addition
of cobalt 2-ethylhexanoate to a cyclohexane solution of triethylaluminum.
The catalyst thus produced had an aluminum/cobalt ratio of 3.25, which
seemed to offer optimal efficiency of the catalyst. According to data
published by Falk [16], this metal ratio gives 100% hydrogenation of
polybutadiene unsaturation in 10 min. Only 0.3 mol% catalyst was nec-
essary, and the reaction was completed at 50°C under only 50 psi of
hydrogen.
     The activity of the catalyst as produced in this laboratory was con-
firmed by performing the same polybutadiene hydrogenation, and simi-
lar results were obtained.
     Falk noted that polyisoprene was hydrogenated more slowly under
these conditions [16, 18], and he demonstrated that by using an alu-
minum/cobalt ratio of 3.45, complete hydrogenation of butadiene un-
saturation could be obtained for a butadiene-isoprene copolymer,
while the amount of isoprene unsaturation was unchanged [18]. Prud'-
homme [19] observed that a 2-h hydrogenation period was required to
effect complete hydrogenation of the isoprene unsaturation using an
aluminum/cobalt ratio of 4.0, at a hydrogen pressure of 50 psi and 5

mol% of catalyst. This was also confirmed in this laboratory, using the catalyst with an aluminum/cobalt ratio of 3.25 described above.

Poly(2,6-di-t-butyl-4-vinylphenol-co-butadiene) and poly(2,6-di-t-butyl-4-isopropenylphenol-co-butadiene) were more difficult to hydrogenate than 1,3-butadiene homopolymer. Seven mol% of triethylaluminum/cobalt 2-ethylhexanoate catalyst was required to effect complete hydrogenation at a hydrogen pressure of 50 psi and a temperature of 50°C. The vinylphenol-isoprene copolymers were also more difficult to hydrogenate than the isoprene homopolymer, requiring 10% of aluminum/cobalt catalyst and 2 h to achieve quantitative hydrogenation.

The presence of the phenolic group in the polymers was the cause of the decreased reactivity for catalytic hydrogenation; the hydroxyl group is capable of complexing with the catalyst, thus reducing its activity. In all cases, several mol% more catalyst than the number of phenol groups in the polymer were required for hydrogenation. For 1,3-butadiene copolymers, one mol% of catalyst was required in addition to the amount of transition metal necessary for the complexation of the phenol group; for isoprene copolymers, 2 to 4 more mol% of catalyst were needed to achieve complete hydrogenation.

One limitation in this hydrogenation reaction is the solubility of the products in the reaction medium. Falk [18] claimed that hydrogenations with aluminum/cobalt catalysts could be carried out in solutions as concentrated as 17 wt%; in our experience and with our copolymers, a concentration of 2 wt% of copolymer in cyclohexane resulted in the precipitation of a black product which occluded some active catalyst.

Workup of the hydrogenated copolymers consisted of vigorous shaking of the black solution with 10% HCl to decompose the catalyst/polymer complex. A pink color developed during this procedure; this was due to the formation of the aquo cobalt complex [20], $[Co(H_2O)_6]^{2+}$.

A stable emulsion was often obtained during this operation, from which the polymer could be isolated by addition of the emulsion to methanol [21].

Analysis of the hydrogenated copolymers by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy indicated no residual unsaturation. The major peak in the ^{13}C NMR spectrum of hydrogenated 1,3-butadiene copolymers, at 30.2 ppm, is due to $-\underline{C}H_2-$, but the spectrum of hydrogenated isoprene copolymers is more complicated. The four major peaks at 38.1, 35.0, 33.4, 25.1, and 20.1 ppm correspond to carbons a, c, b, d, and e, respectively [18].

```
    a     b     c     d
 -CH2-CH-CH2-CH2
        |
        | e
        |
      CH3
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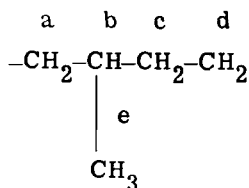
A more serious drawback to the use of Falk's aluminum/cobalt catalyst system to hydrogenate polymeric antioxidants is the purity of the final product. An ash content as high as 2% in the polymers was found. The carbon and hydrogen values found, when corrected for the ash present, agree exactly with the theoretical values. For example, a 2,6-di-t-butyl-4-vinylphenol-1,3-butadiene copolymer (6 mol% phenol) had calculated values for the elemental analysis for C of 85.45 and for H of 14.13. When the values found for C of 83.78 and for H of 13.76 were corrected for the 2.1% ash found, acceptable values for C of 85.54 and for H of 14.05 were obtained.

Other hydrogenation methods were investigated for our vinylphenol-diene copolymers, most importantly the chemical hydrogenation by diimine which generated in situ by thermolysis of p-toluenesulfonhydrazide [22-26]. This method, however, introduced only hydrazide up to 0.3% sulfur and 0.3% nitrogen into the polymer.

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