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^{13}C NMR Study of Poly(2,6-dimethyl-1,4-phenylene oxide)s. Sites of Amine Incorporation

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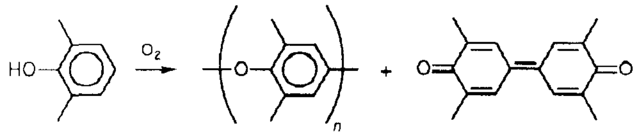
ABSTRACT: During the polymerization of 2,6-dimethylphenol to form poly(2,6-dimethyl-1,4-phenylene oxide), PPO resin, amines in the catalyst are chemically bound to the polymer as a result of side reactions. Details of the sites of binding are revealed by ^{13}C NMR spectroscopy. Unhindered secondary amines are found to be attached via the amino nitrogen to the methyl group at the head end of the polymer chain. In some polymers, secondary amines are also attached but in smaller quantities onto the methyl groups of internal phenylene oxide units. Hindered secondary amines may add similarly but to a smaller extent. Other types of amines (certain tertiary and primary amines) appear to be degraded during the polymerization to amines that can also become bound to the polymer. Spectra of polymers that have been heated to 270 °C no longer display resonances for the terminally bound amines. Internally bound amines, however, still appear to be present after heating. The formation of other types of trace structural units in PPO samples is also discussed.

Introduction

Polymerization of 2,6-dimethylphenol (1) by oxidative coupling produces poly(2,6-dimethyl-1,4-phenylene oxide), PPO resin (2), in high yield as well as a minor product, 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (3).[1] ^{13}C NMR studies have confirmed the basic repeat structure of the polymer,[2] identified the presence of phenolic and phenoxy end groups,[3] shown the formation of biphenyl units when the polymer reacts with 3,[4] and examined chain conformations and relaxations.[2,5] During the early end group studies, alkyl amines from the catalyst were suspected of being bound to the polymer chains, but this could not be confirmed because the resonances of the trace groups in the 25 MHz spectra were too weak to allow full characterization. We have now examined spectra of PPO resins using 50 and 75 MHz spectrometers and have obtained more detailed information on the structures of the polymers. This report describes the spectra of PPO samples prepared with a variety of catalysts. Emphasis is placed on the points of attachment of the amines to the polymers and the types of amines that are bound. Spectra and preparations of relevant model compounds and modified polymers are also presented.



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Experimental Section

^{13}C NMR spectra were measured on Varian XL200 and XL300 spectrometers with deuteriochloroform as solvent and tetramethylsilane as reference. Overnight runs were required for all polymers except the model compounds 5a–e, which required ca. 1 h. ^{1}H NMR spectra were measured on a Varian EM390 spectrometer in deuteriochloroform versus TMS. Gel permeation chromatography was performed on a Waters ALGC GPC with μ-styragel columns (10^5, 10^4, 10^3, 500 Å) with chloroform as eluent. Molecular weight values are based on polystyrene calibrations. 2,6-Dimethylphenol was purified (to 99.9%) by recrystallization from hexane. *N,N′*-Di-*tert*-butyl-1,2-ethylenediamine (DBED) and dimethylbutylamine (DMBA) were distilled before using. The following amines were reagent grade and used without further purification: di-*n*-butylamine (DBA), *N,N,N′,N′*-tetraethylethylenediamine (TEED), *N,N,N′,N′*-tetramethylethylenediamine (TMED), trimethylamine (TMA), diethylamine (DEA), *tert*-butylamine, and morpholine.

PPO resin containing the α-bromo unit (4) was prepared by *N*-bromosuccinimide photobromination[6] of PPO resin (2). To 48 g (0.40 mol of repeat units) of PPO ([η] 0.49 dL/g) in 500 mL of carbon tetrachloride at reflux was added 17.8 g (0.10 mol) *N*-bromosuccinimide while the solution was irradiated with a 150-W flood lamp 10 cm away. After 2.75 h the reaction mixture was filtered while hot (to remove succinimide) and the polymer was precipitated by adding the filtrate to an excess of methanol in a mechanical blender. The precipitate was washed with methanol thoroughly and dried at 60 °C and 10 torr overnight. The product was a pale yellow solid weighing 51 g. Bromine and ^{1}H NMR analyses indicated 18 mol % monobromo units in the polymer.

PPO Resin Containing the α-Amino Unit (5a). To a solution of 10 g (13.2 mol equiv of bromo units) of α-bromo-PPO resin (above) in 100 mL of benzene was added 5 mL (29 mmol) of dibutylamine. After 18 h at 25 °C the hazy reaction mixture was added to excess methanol in a blender to precipitate the polymer. The product was collected on a filter and washed with methanol, water, and then methanol. The dried product weighed 10.2 g; [η] 0.52 dL/g. The nitrogen analysis was consistent with quantitative displacement of bromide.

PPO Resins Containing 5b–e. A procedure similar to the one described above was used with four other amines. The reaction times and extents of conversion are listed in Table I. ^{13}C NMR spectra are presented in Table II.

Synthesis of PPO Resin with a Cu/Morpholine Catalyst. Cuprous bromide (0.192 g, 1.34 mmol) was added to 60 mL of toluene containing morpholine (2.60 g, 29.8 mmol) and 6 g of anhydrous magnesium sulfate. The mixture was stirred, oxygen was bubbled in (0.1 SCFH), and 2,6-dimethylphenol (12.2 g, 0.1 mol) in 36 mL of toluene was added dropwise over a 5-min period. The reaction mixture temperature rose from 25 to 42 °C in 9 min and a water bath was applied to cool the reaction vessel. The temperature gradually dropped to 25 °C (after 43 min) and was maintained at 25 °C. After a total reaction time of 75 min, toluene (75 mL) was added and the mixture was filtered to remove the magnesium sulfate. Methanol (1 L) containing acetic acid (10 mL) was added slowly to the filtrate. The precipitated polymer was washed with methanol and dried at 60 °C (10 torr). Yield, 11.0 g; $\bar{M}_w$ 34 000; $\bar{M}_n$ 12 000.

Polymers from the following catalysts were prepared by published procedures: copper/DBED–DMBA,[7] copper/DBED–DMBA-DBA,[8] copper/DBA,[9] manganese/benzoin oxime,[10] copper/DBED–DMBA–DMA,[11] copper/DBED–DMBA–DEA,[11] copper/TMED–TMA.[12]

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Equilibrated polymers were prepared by heating the polymerization reaction to 80 °C immediately after the polymerization was completed. After 1 h the mixture was cooled to 25 °C and the polymer isolated by the procedure described above.

Poly(2-benzyl-6-methyl-1,4-phenylene oxide) (6) was prepared by the procedure of Hay.[13] A solution of 2-benzyl-6-methylphenol (recrystallized from *n*-hexane), 5.00 g (0.025 mol) in 10 mL of toluene, was added dropwise over 15 min to a vigorously stirred, oxygenated (0.4 SCFM) solution of cuprous bromide (36 mg, 0.25 mmol) and dibutylamine (1.29 g, 10 mmol) in 20 mL of toluene containing 2.5 g of anhydrous magnesium sulfate. The temperature rose from 26 to 39 °C in 25 min and then gradually decreased to 27 °C. After a 2-h reaction time, 1 mL of acetic acid was added and the reaction mixture was filtered. Methanol was added to the filtrate dropwise with stirring and the polymer was collected on a filter, washed with methanol, and dried. Weight, 3.9 g; $[\eta]$ 0.15 dL/g (chloroform, 25 °C); $\bar{M}_w$ 9900; $\bar{M}_n$ 5600.

Heat-Treated Samples. Polymer powders (1–2 g) were compression molded between sheets of Teflon-coated aluminum foil with a heated Carver press. The sample was placed snugly between the preheated platens of the press (at 270 °C) for 30 s. Then ca. 5000 lb of pressure was applied for 1 min. The pressed film was rapidly cooled in air then dissolved in benzene and the PPO was precipitated by adding methanol. The powder was washed thoroughly with methanol and dried at 60 °C and 10 torr. A typical PPO sample prepared with a copper/DBED–DMBA–DBA catalyst contained 900 ppm of bound nitrogen before heating and 500 ppm after heating and precipitation; the intrinsic viscosity increased from 0.50 to 0.58 dL/g. For PPO from a copper/DBED–DMBA–DMA catalyst, nitrogen decreased from 470 to 180 ppm and the intrinsic viscosity increased from 0.54 to 0.59 dL/g. With a copper/DBED–DMBA–DEA catalyst, nitrogen decreased from 580 to 240 ppm and the intrinsic viscosity increased from 0.54 to 0.67 dL/g. With a copper/DBED–DMBA catalyst, nitrogen decreased from 390 to 240 ppm and the intrinsic viscosity increased from 0.52 to 0.53 dL/g.

2-[(Di-*n*-butylamino)methyl]-6-methylphenol (7) was prepared by a method similar to literature procedures.[14] Di-*n*-butylamine (129.2 g, 1 mol; 99+%) was added gradually with cooling to *o*-cresol (108.1 g, 1 mol; 99+%) was added gradually with cooling to *o*-cresol (108.1 g, 1 mol; 99+%) in a three-neck flask equipped with stirrer, thermometer, and condenser. Aqueous formaldehyde (33 g, 1.1 mol; 89.3 g of 37% solution) was added dropwise with cooling to maintain the temperature between 25 and 35 °C. After the addition was finished (15 min) the solution was heated to 90 °C, held at 90 °C for 1 h and then cooled to 25 °C overnight. The aqueous layer was separated, dried over 4A molecular sieves, and then filtered, leaving an organic layer that weighed 249 g. ^{1}H NMR and GC analyses were consistent with a mixture of desired product and trace amounts of starting materials, 2-methyl-4-[(dibutylamino)methyl]phenol and 2-methyl-4,6-bis[(dibutylamino)methyl]phenol.

Attempts to distill the crude product at 0.1 torr caused condensation reactions to occur to produce a mixture that contained **16**. Silylation with BSTFA (0.05 mol to 0.1 mol of crude product, heated at 100 °C for 1 h) followed by distillation produced a fraction containing the trimethylsilyl ether derivatives of **7** and the isomer 2-methyl-4-[(dibutylamino)methyl]phenol in a ratio of 10:1.

Medium-pressure liquid chromatography of a 1-g sample of crude product on silica gel with hexane/ether (3:1) as eluent gave an initial fraction of 99+% pure product **7**, 0.4 g. The second fraction was a mixture of **7** and the side products. ^{1}H NMR of **7**: δ 0.83 (t, 6 H), 1.37 (m, 8 H), 2.20 (s, 3 H), 2.37 (q, 4 H), 3.53 (s, 2 H), 6.4–7.2 (m with a sharp 6.60 resonance, 3 H), 10.1 ppm (br s, 1 H).

2-[(Di-*n*-butylamino)methyl]-4,6-dimethylphenol (8) was prepared from 2,4-dimethylphenol by the procedure used for **7**. The crude product was heated 1 h at 100 °C with bis(trimethylsilyl)trifluoroacetamide (0.5 mol/mol of crude **8**) and then distilled (bp 130 °C at 0.1 torr). The product (5 g) was added to 50 mL of methanol and after 30 min at 25 °C was concentrated on a rotary evaporator. Last traces of solvent were removed with a high-vacuum pump (weight, 3.9 g). ^{1}H NMR: 0.89 (t, J = 7 Hz, 6 H), 1.43 (m, 8 H), 2.21 (s, 6 H), 2.40 (t, J = 7 Hz, 4 H), 3.70 (s, 2 H), 6.63 (m, 1 H), 6.87 (m, 1 H), 10.3 ppm (s, 1 H).

2-[(Dimethylamino)methyl]-4,6-dimethylphenol (9) was prepared by the procedure used for **8** except with anhydrous dimethylamine instead of DBA. Distillation of the crude product (bp 102–104 °C, 0.8 torr) provided a pure sample of **9**. ^{1}H NMR: 2.23 (s, 6 H), 2.31 (s, 6 H), 3.60 (s, 2 H), 6.72 (m, 1 H), 6.97 (m, 1 H), 10.4 ppm (s, 1 H).

2-[(*tert*-Butylamino)methyl]-4,6-dimethylphenol (10) and *N*-*tert*-butyl-3,4-dihydro-2*H*-1,3-benzoxazine (13) were prepared by a procedure similar to the method of Burke.[15] ^{1}H NMR of **10**: 1.23 (s, 9 H), 2.24 (s, 6 H), 3.88 (s, 2 H), 6.15 (s, 1 H), 6.56 and 6.89 ppm (AB pattern, 2 H). ^{1}H NMR of **11**: 1.20 (s, 9 H), 2.16 (s, 3 H), 2.23 (s, 3 H), 4.10 (s, 2 H), 5.01 (s, 2 H), 6.72 (m, 1 H), 6.83 ppm (m, 1 H).

2-[(Di-*n*-butylamino)methyl-^{13}*C*]-4-methoxy-6-methylphenol (12). Formaldehyde-^{13}C (90 atom % ^{13}C), 0.2 g (6.67 mmol) in 1.0 mL of water, was added dropwise over 5 min to a solution of 4-methoxy-2-methylphenol (0.92 g, 6.67 mmol) and di-*n*-butylamine in 2 mL of toluene, which was cooled in an ice–water bath. The mixture was allowed to warm to 25 °C over an hour, heated at 100 °C for 1 h, cooled to 25 °C, transferred to a separatory funnel with ether, and washed with water. The ether layer was extracted with 1.5 N hydrochloric acid (2 × 7.5 mL). The acid phase was washed with ether and neutralized with aqueous 50% sodium hydroxide and aqueous sodium bicarbonate. Ether extraction gave 1.6 g (86%) of **12**. ^{1}H NMR ($CDCl_3$/TMS): 0.89 (t, 6 H), 1.44 (m, 8 H), 2.13 (s, 3 H), 2.95 (d, t, J = 3, 6 Hz, 4 H), 3.70 (d, J = 133 Hz, 3 H), 3.76 (s, 3 H), 6.45 (d, d, J = 3, 5.5 Hz, 1 H), 6.68 (d, J = 3 Hz, 1 H), 10.3 ppm (s, 1 H). ^{13}C NMR ($CDCl_3$/TMS): see Table III.

Synthesis of 4,6-Dimethyl-2-hydroxymethylphenol (16). A 500-mL three-neck round-bottomed flask equipped with a magnetic stir bar, dropping funnel, thermometer, and reflux condenser attached to nitrogen bubbler was charged with 248 g of 5% w/w NaOH (aqueous) (310 mmol) and 30.70 g of 37% w/w formaldehyde solution (aqueous) (378 mmol). There was a temperature rise to 30 °C on mixing. 2,4-Dimethylphenol, 30.5 g, 250 mmol, was added over 30 min from the dropping funnel. The temperature remained at 29 °C throughout the addition. The reaction mixture was stirred at room temperature for 20 h. Glacial acetic acid, 30 mL, was added to neutralize the reaction mixture. Two layers formed and the lower layer was separated as a dark red oil. The oil was chromatographed on silica to yield a pale yellow oil. Recrystallization in benzene/pentane yielded 9.83 g of white crystals. Mp (uncorr) 51–53 °C (lit.[14] 57–8 °C). ^{1}H NMR δ 2.2 (s, 6 H, Ar-CH_3), 4.7 (s, 2 H, Ar-CH_2OH), 6.62 (s, 1 H, Ar H), 6.88 (s, 1 H, Ar H). FTIR (CS_2, 3400–3800 cm^{-1}): absorbances at 3434 cm^{-1} (ϵ = 115) and 3589 cm^{-1} (ϵ = 83).

2-(Ethoxymethyl)-4,6-dimethylphenol (17). The procedure is similar to the processes of Hadlington et al.[17] and Merijan et al.[18] Compound **9** (freshly distilled, 17.9 g, 0.1 mol) was quaternized by stirring with methyl iodide (6.9 mL, 0.11 mol) in 80 mL of ethyl ether at 20 °C for 20 h. The crystalline methiodide was filtered off, washed with ether, and dried, 8.35 g. Mp >155 °C (dec). The filtrate afforded an additional 11.2 g of product on standing. ^{1}H NMR (in DMSO-d_6): 2.24 (s, 6 H), 3.07 (s, 9 H), 3.30 (br, 1 H), 4.50 (s, 2 H), 7.09 ppm (m, 2 H).

The methiodide (3.21 g, 0.01 mol) was heated in 10 mL of absolute ethanol under a nitrogen atmosphere at reflux. Aqueous 50% sodium hydroxide (0.80 g, 0.01 mol) was added dropwise over a 1-min period. After 2 h the reaction mixture was concentrated to a slurry. Chloroform (10 mL) was added, the mixture was filtered to remove sodium iodide, and the chloroform was evaporated. The residue (1.9 g) was distilled, affording pure **17**, bp 76 °C (0.5 torr); weight, 1.46 g (81% yield). ^{1}H NMR: 1.24 (t, J = 7 Hz, 3 H), 2.23 (s, 6 H), 3.57 (q, J = 7 Hz, 2 H), 4.60 (s, 2 H), 6.68 (s, 1 H), 6.89 (s, 1 H), 7.6 (s, 1 H). ^{13}C NMR: see Table IV.

Bis(2-hydroxy-3,5-dimethylphenyl)methane (18) was prepared by the method of von Auwers[19] from 2,4-dimethylphenol and formaldehyde. The product was sublimed and recrystallized (mp 137–138 °C; lit. 145–146 °C). ^{1}H NMR: 2.21 (s, 6

H), 2.25 (s, 6 H), 3.90 (s, 2 H), 6.20 (s, 2 OH), 6.85 (m, 2 H), and 6.97 ppm (m, 2 H).

1,2-Bis(2-hydroxy-3,5-dimethylphenyl)ethane (19). Phenol **9** (3.00 g) was heated to 230 °C for 15 min under nitrogen. Medium-pressure liquid chromatography (10% ethyl acetate in hexane on silica gel) of the nonvolatile residue afforded 1.9 g of crystalline material containing 32% **19**. Rechromatography (5% ethyl acetate in hexane on silica gel) followed by recrystallization from hexane afforded pure **19**, mp 160–161 °C (lit.[20] 166–167 °C). ^{1}H NMR: 2.26 (s, 12 H), 2.80 (s, 4 H), 5.67 (s, 2 H), 6.89 ppm (s, 4 H). Mass spectrum: 270, 269, 148, 135 (base peak), 91.

2,4-Bis(2,6-dimethylphenoxy)-6-methylanisole (22). A mixture of 2,6-dimethylphenol (13.4 g, 0.11 mol), potassium *tert*-butoxide (12.3 g, 0.11 mol), and 50 g of anisole was heated to 150 °C under nitrogen to remove *tert*-butyl alcohol in a Dean-Stark trap. The mixture was cooled to 120 °C and 2,4-dibromo-6-methylanisole (14.0 g, 0.05 mol) and cuprous chloride (1.0 g, 0.01 mol) were added. The mixture was heated at reflux for 2 h and then cooled. The reaction mixture was triturated with pentane and then with acetone. The acetone was evaporated and the oily residue was chromatographed (medium-pressure liquid chromatography: silica gel/hexane). Compound **22** eluted as the second main fraction (190 mg). Mass spectrum: *m/e* 362 (base peak), 347, 332, 319, 242, 252, 211. ^{1}H NMR: 2.10 (s, 6 H), 2.20 (s, 6 H), 2.23 (s, 3 H), 3.97 (s, 3 H), 6.53 (s, 1 H), 7.0–7.1 ppm (m, 7 H).

2-Amino-3,5-dimethyl-1-(2,6-dimethylphenoxy)-4-phenoxybenzene. To a 300-mL round-bottomed flask equipped with magnetic stir bar were added 2-nitro-3,5-dimethyl-1-(2,6-dimethylphenoxy)-4-phenoxybenzene[21] (7.66 g, 21 mmol), absolute EtOH (70 mL), and 325 mesh size iron powder (7.77 g, 139 mmol). Concentrated HCl (1.6 mL) was added over 5 min in 0.4-mL aliquots. The reaction mixture stirred at reflux for 8 h, was cooled and neutralized with saturated Na_2CO_3, and was filtered to remove the inorganic salts. The crude reaction was purified by column chromatography (200 g of silica gel) and eluted with 5% diethyl ether in hexane to yield a white solid, 6.18 g (88%). ^{1}H NMR ($CDCl_3$/TMS): 6.66–7.40 (m, 8 H, Ar″ H and Ar′ H), 6.02 (s, 1 H, Ar H), 3.80 (s, 2 H, NH_2), 2.17 (s, 6 H, Ar′CH_3), 2.00 (s, 3 H, ArCH_3), 1.83 (s, 3 H, ArCH_3). ^{13}C NMR: 158.3, 151.4, 144.9, 141.9, 132.5, 131.3, 129.4, 128.9, 124.8, 120.9, 119.9, 117.0, 114.5, 111.5, 16.2, 15.8, 10.5. IR (KBr): 3360, 3450 (NH_2).

2-(Dibutylamino)-3,5-dimethyl-1-(2,6-dimethylphenoxy)-4-phenoxybenzene (23). To a 25-mL round-bottomed flask equipped with a magnetic stir bar and a septum attached to a nitrogen bubbler were added 2-amino-3,5-dimethyl-1-(2,6-dimethylphenoxy)-4-phenoxybenzene (0.1050 g, 0.31 mmol) and freshly distilled THF (10 mL). The contents were cooled to −5 °C with an ice/salt bath and *n*-BuLi (0.134 mL of 2.5 N, 0.335 mmol) was added with a syringe. After 15 min of stirring at this temperature, 1-iodobutane (0.38 mL, 61.6 mg, 0.335 mmol) was added and after 30 min this two-step process was repeated. The reaction mixture was stirred at room temperature for 18 h. The solvent was removed in vacuo and the crude product was purified by column chromatography (30 g of silica gel), eluting with a gradient from 100% hexane to 100% diethyl ether. ^{1}H NMR: 6.7–7.4 (m, 8 H, Ar′ H and Ar″ H), 5.92 (s, 1 H, Ar H), 3.10 (t, 4 H, NCH_2), 2.10 (s, 6 H, Ar′CH_3), 2.06 (s, 3 H, ArCH_3), 1.82 (s, 3 H, ArCH_3), 1.55 (m, 8 H, β- and γ-CH_2), 0.90 (t, 6 H, CH_3). ^{13}C NMR: 157.4, 153.3, 149.9, 144.2, 131.3, 129.4, 129.0, 124.9, 120.9, 114.5, 111.1, 48.6, 29.6, 20.1, 16.3, 16.1, 13.8, 12.0.

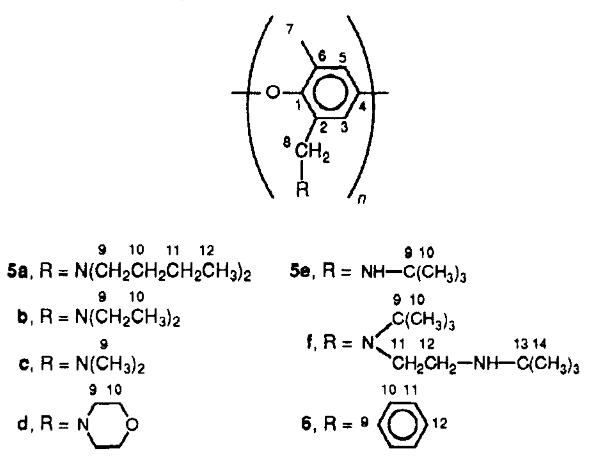
3-[(Di-*n*-butylamino)methyl]-3′,5,5′-trimethyl-4,4′-biphenol (41) was prepared by the method of Hay[22] from **3** and DBA in *N*-methylpyrrolidone (NMP) at 25 °C for 17 h. ^{13}C NMR: 14.0, 20.6, 28.4, 53.1 (butyl); 15.9, 16.0 (ArCh$_3$); 58.3 (ArCH_2); 121.6, 123.3, 124.3, 124.9, 126.8, 128.0, 131.6, 133.5, 151.2, 155.3 ppm (aryl C's).

Quinone Methide Trimer 45. A sample of **45** (R = *tert*-butyl) from Dr. D. A. Bolon[23] was analyzed by ^{13}C NMR. The spectrum was consistent with the proposed structure: 15.3, 16.1, 16.5 (vinyl- and arylmethyls); 22.8, 27.2, 32.8 (methylenes); 25.4 (vinyl-*tert*-butylmethyl 31.6 (both aryl-*tert*-butylmethyls); 33.8, 34.1, 39.7 (*tert*-butyl); 79.7, 84.6 (aliphatic ether carbons); 118.7, 122.6, 123.0, 124.6, 125.2, 125.7, 127.0, 129.5, 135.6, 136.9, 141.9, 145.5, 149.4, 149.9 (aryl and vinyl), 195.9 ppm (carbonyl).

Table I
Reaction of Amines with Bromo Polymer 4 in Benzene at 25 °C

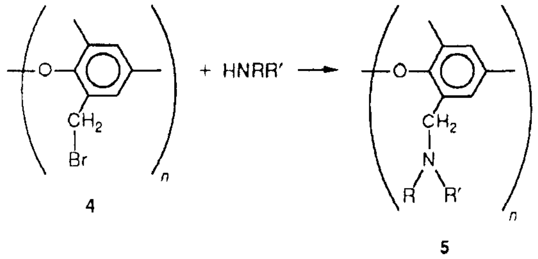
amine	product	rctn time, h	convsn, %
morpholine	**5d**	4	100
diethylamine	**5b**	4	100
dimethylamine	**5c**	5	>95
dibutylamine	**5a**	18	100
tert-butylamine	**5e**	18	70
DBED[a]	**5f**	18	~50
DBED[a]	**5f**	96	100

[a] *N,N*′-Di-*tert*-butyl-1,2-ethylenediamine.



Results and Discussion

Model Compounds. Polymers with Pendent Amino Groups. A series of PPO resins with pendent amino groups was prepared to measure the ^{13}C NMR spectra of alkyl amino groups located on the methyl groups of internal repeat units of the polymer backbone. The amino groups were introduced by reaction of the appropriate amine with a partially methyl-brominated polymer:[6]



By using a polymer with 18% of its repeating units brominated, the amino units in the product were sufficiently concentrated for convenient NMR analysis yet were adjoined by normal PPO repeating units at the 1- and 4-positions. The reactions were run with excess amine to scavenge hydrogen bromide. The reaction times varied with the type of amine since the rates were slower with the more hindered amines (Table I).

The chemical shifts of the polymers with alkyl amino groups and one with a benzyl group are summarized in Table II.

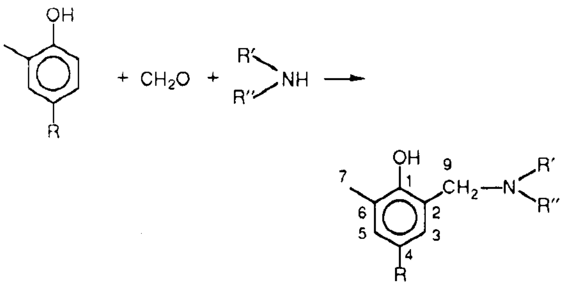
The assignments are consistent with expected peak intensities and with analogies to literature values for related compounds.[2-4,24] The chemical shifts at C-1 and C-4 are typical for poly(phenylene oxide)s.[2,4] The downfield shift of C-4 with respect to C-1 reflects the stronger interaction of the C-4 carbon with the adjacent oxygen than occurs between the C-1 carbon and its adjacent oxy-

Table II
^{13}C Chemical Shifts of Substituted PPO Resins

	chemical shift, ppm								
carbon	**2**	**4**	**5a**	**5b**	**5c**	**5d**	**5e**	**5f**	**6**
1	145.4	145.9	145.0	145.0	145.1	145.3	145.0	143.6	144.9
2	132.4	132.7	135.1	134.8	133.2	132.6	135.6	138.4	135.6
3	114.5	117.9	113.1	113.8	112.5	~113.4	113.0	112.9	115.1
4	154.7	154.9	155.2	154.9	154.9	154.8	155.4	154.9	154.9
5	114.5	114.9	115.7	114.8	115.7	115.4	117.7	~114.0	114.5
6	132.4	132.1	~132.5	~132.4	132.0	~132.2	~132.5	132.1	132.8
7	16.7	~16.7	~16.7	~16.7	16.7	~16.7	~16.7	16.5	16.8
8	16.7	28.1	52.5	51.4	57.9	56.4	42.7	52.8	36.3
9			54.0	47.0	45.4	53.3	50.6	54.9	139.9
10			29.5	11.9		66.8	29.0	27.0	129.0
11			20.5					49.2	128.2
12			14.0					42.7	125.9
13								49.9	
14								29.0	

gen.[25] Attachment of the amino group to a methyl group of the repeat unit increases the inductive effect of the substituent. The increased deshielding at C-2 causes a downfield shift ranging from 0.2 ppm in **5d** to 6 ppm in **5f**. The assignments of shifts for C-3 and C-5 are tentative since in many cases their differences are small. The chemical shifts of the alkyl groups of the amines and the benzylic methylene groups of attachment differ considerably from the corresponding carbons of the repeat units and the corresponding secondary amines. For example, the chemical shifts for C-9 and C-10 of the *unit* **5a** are at 54.0 and 29.5 ppm, respectively, while in DBA the analogous carbons are at 50.1 and 32.7 ppm. Such effects for increased substitution on an amino nitrogen are well-known.[26]

Models of End Groups and Related Structures. To determine where the chemical shifts of terminal aminomethyl groups in PPO resins should occur, a series of model (aminomethyl)phenols (**7**–**13**) was prepared. Several models of other types of end groups (**15**–**17**) and models for internal units that could arise from side reactions (**14**, **18**, and **19**) were also prepared. Most of the (aminomethyl)phenols were prepared by the Mannich reaction.[14] When secondary amines were used, the expected products were isolated in high yield:



7: $R' = R'' = \overset{10}{C}H_2\overset{11}{C}H_2\overset{12}{C}H_2\overset{13}{C}H_3$; $R = H$

8: $R' = R'' = \overset{10}{C}H_2\overset{11}{C}H_2\overset{12}{C}H_2\overset{13}{C}H_3$; $R = \overset{8}{C}H_3$

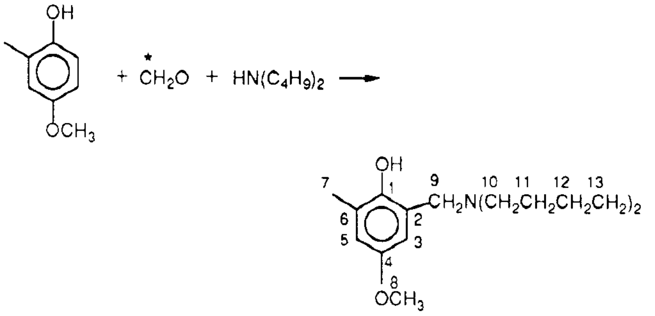
9: $R' = R'' = \overset{10}{C}H_3$; $R = \overset{8}{C}H_3$

10: $R' = \overset{10}{C}(\overset{11}{C}H_3)_3$; $R'' = H$; $R = \overset{8}{C}H_3$

11: $R' = \overset{14}{C}H_3$; $R'' = \overset{10}{C}H_2\overset{11}{C}H_2\overset{12}{C}H_2\overset{13}{C}H_3$; $R = \overset{8}{C}H_3$

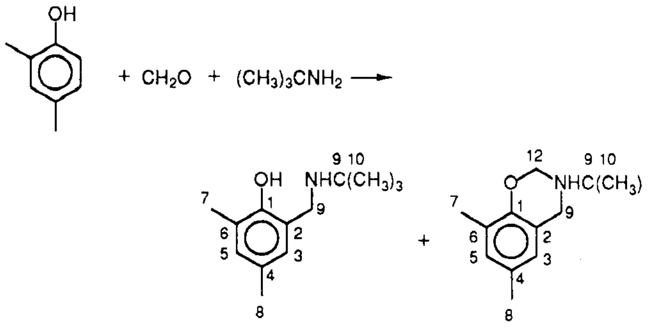
Two minor impurities in the preparation of **7**, the 4-substituted isomer and the 2,4-disubstituted product, were separated from **7** by chromatography. Compounds **7** and **8** decomposed during distillation but the trimethylsilyl ether derivatives were stable during distillation. They were deprotected by dissolution in methanol.

A labeled (aminomethyl)phenol, **12**, was prepared by the reaction of 90 atom % formaldehyde-^{13}C and dibutylamine with 4-methoxy-2-methylphenol. The 4-methoxy-2-methylphenol was prepared by methylation of 4-methoxyphenol.



12

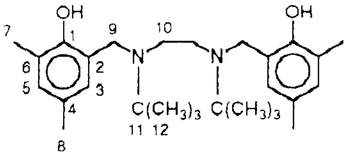
Mannich reactions with primary amines are known to form dihydrobenzoxazines.[15] With *tert*-butylamine, a mixture of the desired product **10** and the dihydrobenzoxazine **13**[15] was formed. Compound **10** was isolated from



10 **13**

the reaction mixture as a solid and was purified by recrystallization.

A variety of reactions was used to prepare many of the other models. Compounds **14** and **15** were prepared from 2,4-dimethylphenol and *N*,*N*′-di-*tert*-butyl-1,3-imidazolidine.[27] Alcohol **16** was made by the hydroxymethylation of 2,4-dimethylphenol.[16] Ether **17** was prepared by heating quaternized **9** with ethanol, presumably by addition of ethanol to an intermediate quinone



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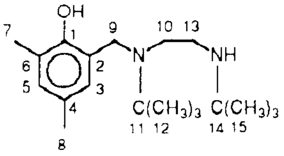

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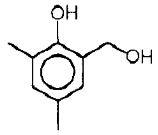

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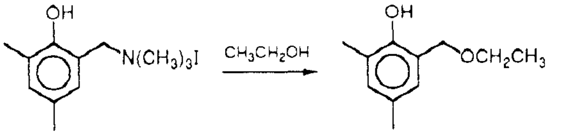

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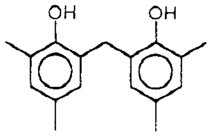

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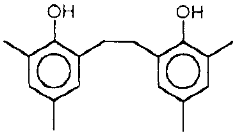

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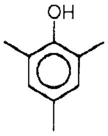

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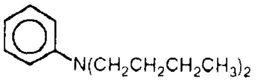
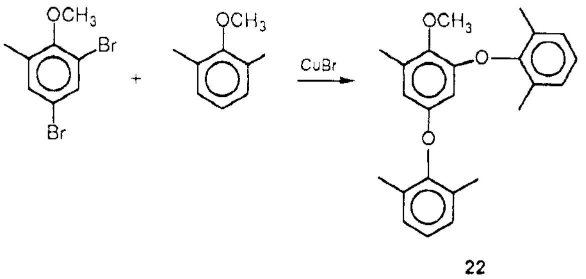


21

methide.[17,28] Bisphenol **18** was prepared from formaldehyde and 2,4-dimethylphenol.[21] Bisphenol **19** was isolated from the products that arose from the pyrolysis of **8**. *N,N*-Di-*n*-butylaniline (**21**) and 2,4,6-trimethyphenol (**20**) were commercial samples. Triether **22** was prepared in low yield by the Ullmann ether synthesis from 2,4-dibromo-6-methylanisole:



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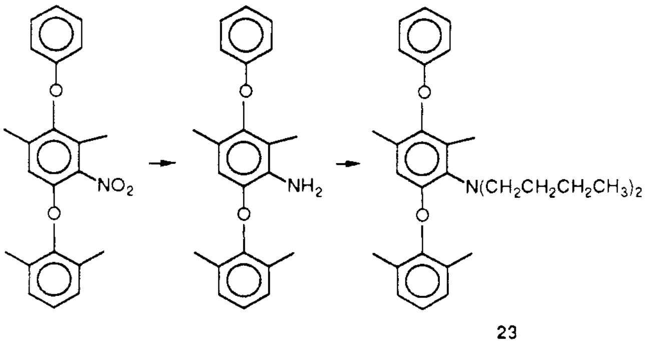
Amine **23** was prepared by the sequence



23

Table III
^{13}C Chemical Shifts of Various Mannich Base Phenols

	chemical shift, ppm							
carbon	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	156.6	154.0	153.5	156.7	153.5	149.8	151.0	153.8
2	121.5	121.3	120.7	130.0	120.7	122.0	128.6	122.8
3	126.2	126.5	126.1	128.8	126.2	111.5	124.2	126.6
4	118.4	127.1	127.1	127.5	127.0	151.7	125.3	127.8
5	129.8	130.4	130.2	132.9	130.1	114.6	129.0	130.3
6	124.6	124.4	-124.1	125.2	124.1	125.3	122.07	124.6
7	15.8	15.7	15.3	18.3	15.4	15.8	15.5	15.5
8	58.4	20.5	20.2	23.1	20.2	55.5	20.5	20.4
9	53.3	58.4	62.7	48.7	61.3	58.1	45.4	55.7
10	28.8	53.3	44.2	53.6	56.7	52.9	78.9	51.6
11	20.7	28.7		31.2	28.9	28.3	54.0	54.5
12.	14.0	20.7			20.2	20.4	28.1	26.1
13		14.0			13.7	13.9		
14					40.7			

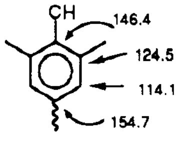
Table IV
^{13}C Chemical Shifts of Various Phenols and Amines

	chemical shift, ppm							
carbon	**1**	**14**	**16**	**17**	**18**	**19**	**20**	**21**
1	153.7	153.6	151.9	152.2	148.6	149.6	149.7	148.2
2	124.4	122.4	125.1	125.1	126.3	127.1	122.8	111.9
3	129.0	125.5	125.9	126.0	128.6	128.1	128.?	129.2
4	120.2	127.3	128.8	128.3	129.9	129.5	129.?	115.3
5	129.0	129.7	131.4	131.2	129.8	129.6	128.9	129.2
6	124.4	124.4	124.0	121.4	123.9	123.2	122.8	111.9
7	16.4	15.4	15.5	15.6	15.9	15.7		50.8
8	16.4	20.2	20.3	20.4	20.3	20.3		29.6
9		54.2	64.6	72.4	31.1	32.0		20.4
10		52.1		66.1				14.1
11		56.0		15.1				
12		26.3						
13		42.4						
14		50.0						
15		28.5						

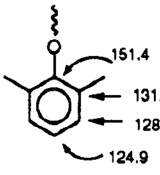
The ^{13}C NMR spectra of the Mannich base phenols **7–14** are presented in Table III. Spectra of related phenols and amines (compounds **1** and **15–21**) are presented in Table IV. These spectra will be used to estimate chemical shifts of possible anomalous structures in PPO samples. The spectra of **22** and **23** are presented in the Experimental Section.

The assignments for the resonances in Tables III and IV are based on the additivity effects of substituents on aromatic rings,[29] on spectra of related compounds,[17,29,30] and on peak intensities. Assignment at the 2-position is aided by the spectrum of **12**. The ^{13}C-enriched methylene adjacent to C-2 results in a doublet (J = 46 Hz) for C-2 centered at 122.0 ppm. The resonance for C-6 in the spectrum of **12** is at 125.3 ppm. Thus, it appears that hydrogen bonding of the amine to the phenolic hydroxyl markedly affects the inductive effects of the substituents at C-2 and C-6: As a result C-2 is more deshielded than C-6 and their relative positions in the (aminomethyl)phenols in Table III are the reverse of those of the aminomethyl ethers in Table II. The resonances at 111.5 and 114.6 ppm in the spectrum of **12** are assigned to C-3 and C-5, respectively. The broader of the two resonances is assigned to C-3, since long-range coupling in benzylic systems produces a larger value for $J_{3,9}$ than for $J_{5,9}$. For some compounds in Tables III and IV the assignments at C-2 and C-6 and also at C-3 and C-5 are tentative because the differences in chemical shifts are small.

Polymer Spectra. A typical ^{13}C NMR spectrum of a PPO resin is characterized by five intense resonances for the carbons of the basic repeating units and a larger number of weak resonances. Some of the weak resonances are due to $^{13}C-^{13}C$ coupling of the carbons in the repeating units. The intensities of these resonances (each peak is 0.5% of the adjacent repeat unit carbon peaks) are frequently similar in intensity to many of the other weak resonances in the spectrum. Sometimes associated with the intense peaks in 50-MHz spectra are weak peaks that are located 1.6 ppm upfield. They are believed to be quadriphasic images of the adjacent intense peaks. Analogous peaks are not seen in 75-MHz spectra. Other resonances can arise from "normal" head an tail end groups. Characteristic values[3,4] are

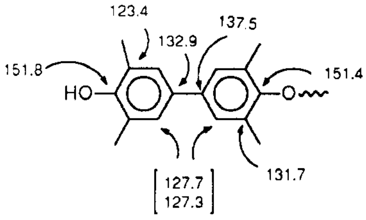


24
"normal" head unit



25
tail unit

When biphenol units are present in the polymer as a result of reaction of "normal" head end units with diphenoquinone 3 additional resonances occur. Tentative assignments for the resultant end group, **26**,[4] are



25

In addition to the weak resonances described above there are additional weak peaks in the aliphatic and aryl regions, which vary in number, intensity, and chemical shift depending on the polymerization catalyst and polymerization reaction conditions. Many of these resonances can be attributed to alkylamino groups attached to the polymer chain. The presence of nitrogen in PPO samples has been described[31] and is supported in our studies by Kjeldahl analyses, which show trace quantities of nitrogen in polymers even after rigorous purification by extraction and reprecipitation. The nitrogen contents frequently range from 500 to 1000 ppm, which corresponds to approximately one nitrogen atom per polymer molecule. Since amines associated with the catalyst are the only source of nitrogen in these polymerization systems, these amines appear to have been bound to the polymer during polymerization. The ^{13}C NMR resonances that are consistent with the presence of covalently bound amines in the polymers are described below, along with a description of the specific catalyst system used in the synthesis.

Polymer from the Cu/DBED-DMBA-DBA Catalyst. The Cu/DBED-DMBA-DBA catalyst[7] is a combination of CuBr, *N*,*N'*-di-*tert*-butylethylenediamine (DBED), dibutylamine (DBA), and butyldimethylamine (DMBA). The mole ratio of these components for the polymer described here was 1:2:8.5:40, respectively, per 900 2,6-dimethylphenols. The catalyst is of particular interest because it has high activity and retains activity when water forms during the polymerization. A minor nitrogen-containing component in this catalyst is the quaternary salt Adogen 464 (tricaprylmethylammonium chloride). Its low concentration and chemical inertness do not make it a major source of the nitrogen-containing groups that are bound to the polymer. The DBA, however, does appear to be the main source of nitrogen in the polymer and is described in detail below. Conditions that can lead to DBED and DMBA bound to the polymer will be mentioned later in this report.

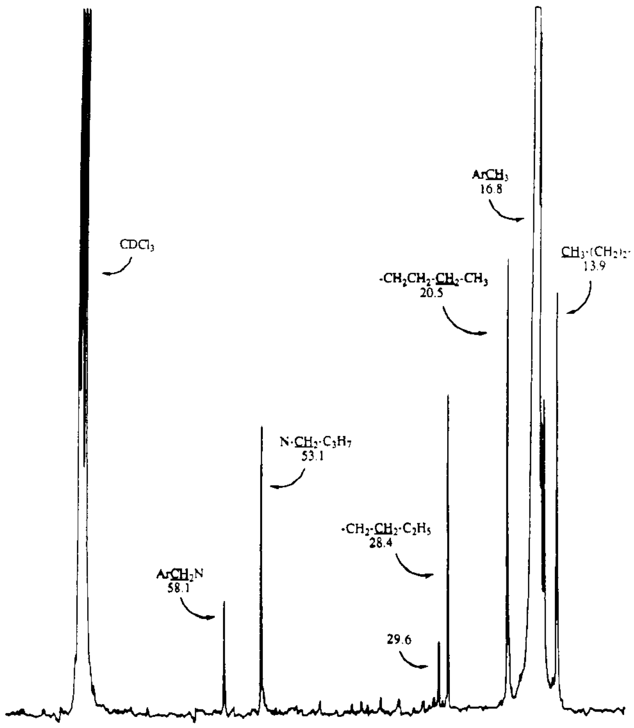


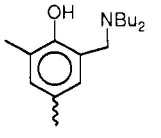
Figure 1. Aliphatic region of the ^{13}C NMR spectrum of a copper/diamine PPO.

Table V
Weak Alkyl ^{13}C NMR Resonances

material	chemical shifts, ppm				
Cu/diamine PPO	58.1	53.1	28.4	20.5	13.9
7	58.4	53.3	28.8	20.7	14.0
8	58.4	53.3	28.7	20.7	14.0
5a	52.5	54.0	29.5	20.5	14.0
21		50.8	29.6	20.4	14.1
DBA		50.1	32.7	20.8	14.1

The aliphatic region of a ^{13}C NMR spectrum of PPO from the Cu/DBED-DMBA-DBA catalyst is shown in Figure 1. Five resonances compare closely in chemical shift and relative intensity with model compounds 7 and 8 but differ significantly from models **5a**, 18, and DBA for all but two resonances (Table V). Only one unassigned resonance (at 29.6 ppm) remains in the aliphatic region and it is relatively weak. Other PPO samples, which are described below, also show a resonance near 29.6 ppm; its origin will be discussed later in this report.

Since all the major aliphatic resonances closely match compounds 7 and 8, the presence of a head end group with structure **27** is strongly suggested. From the intensities of the aliphatic peak, **27** would appear to be the predominant head end group. From the lack of other *n*-butyl resonances, the quantity of dibutylamino groups



27

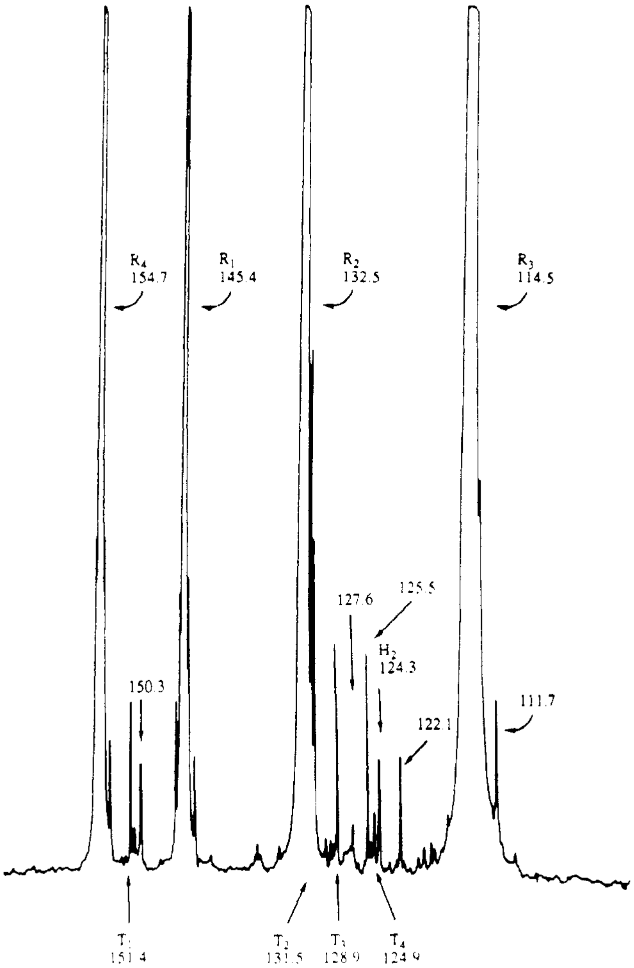
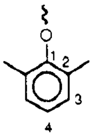


Figure 2. Aromatic region of the ^{13}C NMR spectrum of a copper/diamine.

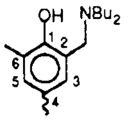
Table VI
Aryl ^{13}C Resonances for Cu/DBED–DBA PPO

observed resonances			
intense main repeat unit	principal minor	tail units **25**[b]	proposed for **27**[b]
154.7 C-4			
	151.4	151.4 C-1	
	150.2		150.2 C-1 (or -6) 150.1 C-6 (or -1)
145.4 C-1			
132.5 C-2			
	131.5	131.4 C-2	
	128.9	128.9 C-3	
	127.6		
	125.5		125.5 C-6
	124.9	124.9 C-4	
	124.3[a]		
	122.1		122.1 C-2
114.5 C-3			
	111.7		111.5 C-3

[a] Head unit (C-2). [b]



25[b]



27[b]

in other locations, e.g., on internal methyl groups or at the 3-position of any aryl rings, is much less than on the head end group methyls.

The aromatic region of a ^{13}C NMR spectrum of the Cu/DBEDA-DBA polymer is shown in Figure 2. In addition to the intense main repeat unit resonances a number of weak resonances are present. Many of these resonances can be attributed to normal tail units and to head units with structure **27** (Table VI). The proposed values for **27** were calculated by adding the differences in chemical shifts at each carbon between compounds **7** and **1** to the chemical shifts of the "normal" PPO head end group **22**. The only principal minor resonance that is unassigned is at 127.6 ppm. This could arise from the terminal hydroxy biphenyl unit **26** (or an analogous internal biphenyl unit) in the polymer as a result of C–C coupling.

Thus, all of the principal major and minor aryl and aliphatic resonances in this high molecular weight PPO sample can be attributed to basic repeat units, normal tail units, a small amount of C–C coupling, and amine-containing head units. Lower molecular weight polymers made with the same catalyst but by stopping the reaction early differ in two respects. The normal head units, **24**, are now apparent from resonances at 146.4 and 124.5 ppm (those at 154.7 and 114.1 ppm are obscured by intense main repeat unit resonances) and the resonances due to the amino end, **27** are weaker.

Equilibrated Cu/DBED–DBA Polymers. When a toluene solution of Cu/DBED–DBA polymer and **3** is heated (or a polymerization reaction mixture after polymerization is over), redistribution reactions[32] occur and **3** undergoes a redox reaction with the polymer that incorporates **3** into the polymer backbone as the moiety **26**.[4] The trace peaks in a ^{13}C NMR spectrum of a polymer that has undergone such an equilibration with **3** differ from the spectrum of polymer isolated immediately after polymerization. In the aromatic region resonances at 127.5, 137.3, and 150.8 ppm can be attributed to structure **26** and to a similar structure with aryloxy units on both ends of the biphenyl group. In the aliphatic region resonances at 53.9, 52.5 (often a weak shoulder on the 53.1 resonance of **27**), 29.3, 20.3, and 13.9 ppm are similar to values for an internal (dibutylamino)methyl group as seen in the model polymers bearing structure **5a** (with resonances at 54.0, 52.5, 29.5, 20.5, and 14.0 ppm). Thus it appears that during the equilibration with **3**, not only is **3** incorporated but also a redistribution reaction occurs that relocates terminal amino units of type **27** into the backbone to form the internal amino units **5a**.

Commercial Cu/DBED–DBA PPO resins appear to have undergone equilibration and incorporation of **3** during their preparations because their spectra contain a small amount of internal amino units **5a** as well as the more prevalent terminal amino units **27** and biphenyl moieties **26**.

Polymer from a Cu/DBA Catalyst. The principal components of the catalyst are cuprous bromide and DBA with the DBA used in a relatively large amount.[9] A typical catalyst ratio is 1:40:200 for CuBr/DBA/1. The resultant polymers normally have more bound nitrogen than polymers made with the Cu/DBED–DBA catalyst (approximately 1200 ppm).

The aliphatic region of a ^{13}C NMR spectrum of a commercial Cu/DBA PPO (Figure 3) is similar to the spectrum for an equilibrated Cu/diamine PPO. It contains a number of weak resonances at 53.9, 52.5, 29.3, 20.3, and 13.9 ppm, which are very similar to those due to the internal (dibutylamino)methyl groups **5a** in the equilibrated polymer, as well as more intense resonances at 58.1, 53.1, 28.3, 20.5 and 13.8 ppm for the terminal amino units **25**. A cluster of very weak peaks between 29 and

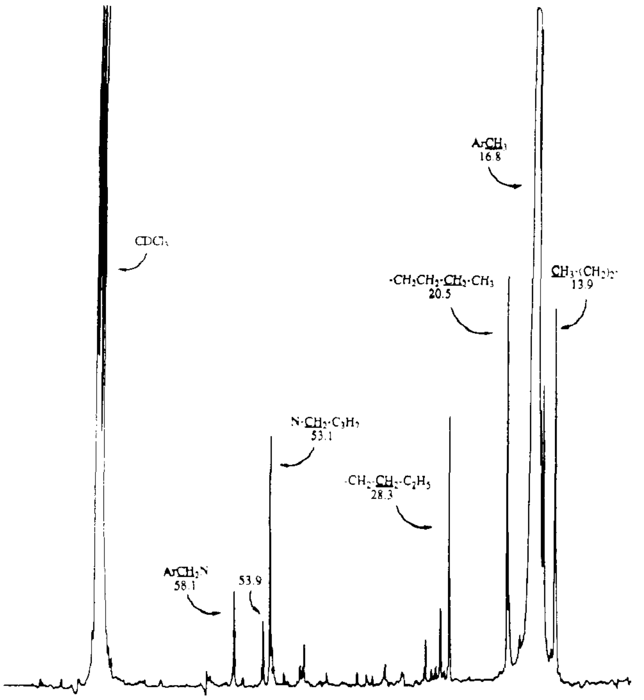


Figure 3. Aliphatic region of the ^{13}C NMR spectrum of a copper/DBA PPO.

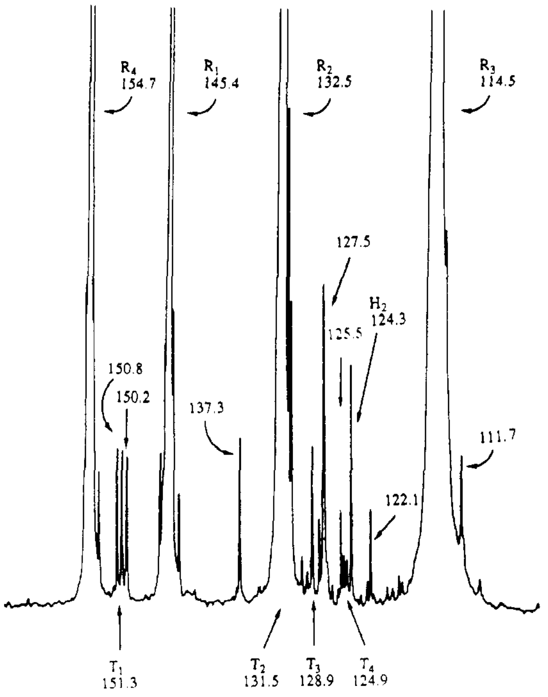


Figure 4. Aromatic region of the ^{13}C NMR spectrum of a copper/DBA PPO.

35 ppm and one at 48 ppm are unassigned. Very weak peaks between the normal aromatic region and aliphatic region occur at 91 and 96 ppm in this spectrum and in spectra of various other types of PPO resins. This region will be discussed later in this report.

The aromatic region of the spectrum (Figure 4) contains all of the resonances that appear in Figure 2 for the Cu/DBEDA-DMBA-DBA resin as well as a number of additional weak resonances. Several resonances (127.5, 137.3, and 150.8 ppm) can be assigned to biphenyl units, both in a terminal position such as **26** and possibly internal (i.e., with an ether linkage on both ends).

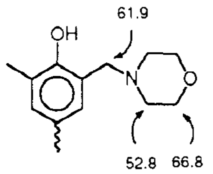
Thus, the commercial Cu/DBA PPO resins resemble the commercial Cu/DBED-DMBA-DBA PPO resins by containing internal (dibutylamino)methyl groups **5a** as well as terminal ones on the head unit of the PPO chain **27**.

The ^{13}C NMR spectrum of a laboratory sample of the Cu/DBA PPO resin resembles the spectrum of the Cu/DBED-DMBA-DBA PPO sample more closely than it resembles the spectrum of the commercial Cu/DBA PPO resin. The principal feature is a much smaller quantity of internally bound amine **5a** in the laboratory material than in the commercial material.

PPO from a Mn/Benzoin Oxime Catalyst. The Mn/benzoin oxime catalyst contains manganous chloride, benzoin oxime, sodium hydroxide, methanol, and dibutylamine.[10] The catalyst is extremely active and can produce high molecular weight PPO rapidly at levels of less than a 1:2:1000 ratio of Mn/benzoin oxime/**1**.

The ^{13}C NMR spectrum of this polymer is very similar to the Cu/DBED-DMBA-DBA PPO spectrum (Figures 1 and 2). In the aliphatic amine region, sharp resonances at 58.2, 53.2, 28.4, 20.5, and 13.9 ppm (compare with Table V) indicate an amine is at the head end of the chain **27**. Very weak 54.0 and 29.3 ppm resonances correspond to ca. 10% of the amines located internally (**5a**). The aromatic resonances also fit the pattern of the Cu/DBED-DMBA-DBA polymer. A very weak resonance at 94.2 ppm and even weaker one at 96 ppm are also present.

Cu/Morpholine PPO. The use of morpholine instead of DBA in a Cu/DBA catalyst system produces a polymer with the secondary amine primarily on the head unit. The following assignments are consistent with the head unit **28**:



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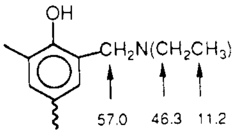
Several very weak resonances with chemical shifts that are almost identical with those of **5d** in Table II (δ 53.4, 56.9, and 66.9 ppm) are consistent with only a small amount of internally bound amine being present.

Polymers Containing DEA and DMA. Substitution of diethylamine for DBA[11] in the Cu/DBED-DMBA-DBA catalyst produces a polymer with a ^{13}C NMR spectrum analogous to the corresponding DBA system except that the aliphatic region (Figure 5) shows incorporation of diethylamino units instead of dibutylamino units and they are primarily on the head end group, i.e., **29**:



29

With dimethylamine, instead of DBA, the spectrum is consistent with a polymer with a dimethylamino group

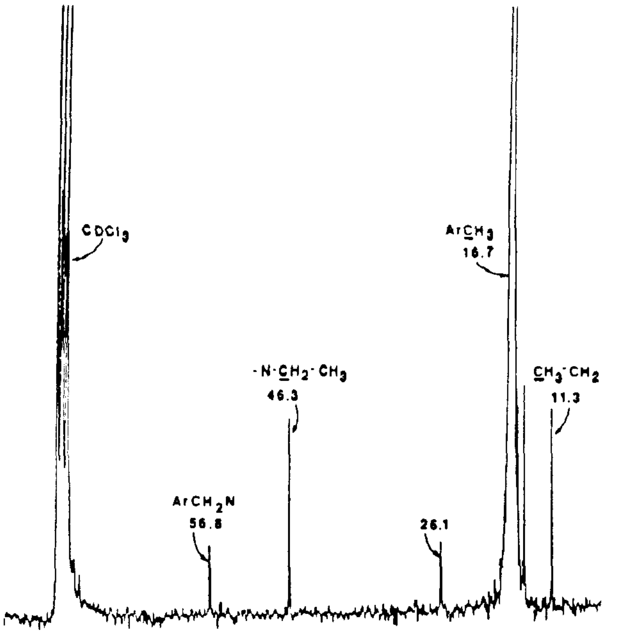
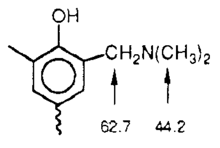


Figure 5. Aliphatic region of the ^{13}C NMR spectrum of a copper/DBED-DMBA-DEA PPO.

on the head end group, 30.



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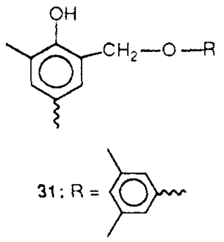
Both of these polymers display a very weak 96 ppm resonance.

PPO Resins Made without Unhindered Secondary Amines Present. A series of polymers was prepared from catalysts that did not contain DBA or other relatively unhindered secondary amines. In general, the weak resonances in their ^{13}C NMR spectra differ widely in the nonaromatic region. In the aromatic region only a few resonances other than normal tail units are observed. The spectra are described below for polymers from a variety of catalyst systems.

$MnCl_2$/Benzoin Oxime. Only resonances for tail end groups and one at 68.9 ppm with an intensity comparable to the tail end group resonances are found. The methylene group of a benzyl ether linkage 31 occurs in this region; however, no additional supporting evidence for such a group is available. The possibility of units 32 or 33 seems unlikely since the characteristic benzyl alcohol resonance normally occurs more upfield (64.6 ppm in 15 and 64.4 ppm in benzyl alcohol) and the methoxy group resonance (~58 ppm) is not seen.



31: R =

32: R = H

33: R = CH_3

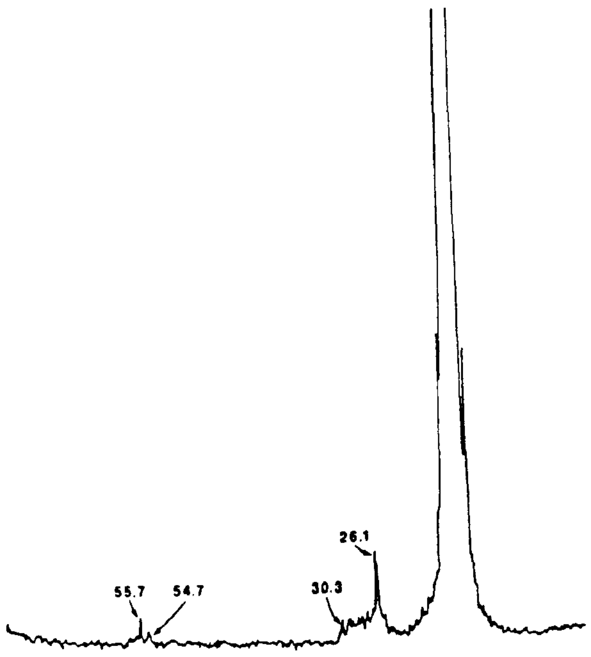
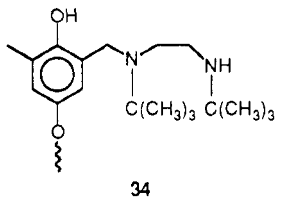


Figure 6. Aliphatic region of the ^{13}C NMR spectrum of a copper/DBEDA PPO.

CuCl/*N,N,N′,N′*-Tetraethyl-1,2-ethylenediamine. This catalyst at low temperatures produces a polymer with a low nitrogen content (230 ppm) and with such a high molecular weight (e.g., $[\eta]$ 1.9 dL/g) that only one tail end group resonance (at 128.9 ppm) is seen by ^{13}C NMR. Only one additional minor resonance (at 96.1 ppm) is found and it is also very weak.

CuBr/DBED. When DBED is the only amine used with CuBr at the normal catalyst ratio for the Cu/DBED-DBA reaction, the polymerization is extremely slow. With higher concentrations of DBED (Cu:DBED:1 = 1:20:100) the reaction is faster and nitrogen is found in the polymer. A sample prepared at 40 °C contains ca. 910 ppm nitrogen and displays a cluster of at least ten weak ^{13}C resonances between 25 and 30 ppm with the strongest one at 26.1 ppm (Figure 6). Additional weak resonances occur at 54.7, 55.7, and 97 ppm. The resonances at 26.1, 54.7, and 55.7 ppm are similar to resonances in 14 and 15 and are consistent with some of the nitrogen bound as an intact DBED moiety (either 34 or 35 or both). Degradation products from DBED are probably incorporated too, which contribute to the other weak resonances. The involvement of DBED is currently under study and will be described in a later report.



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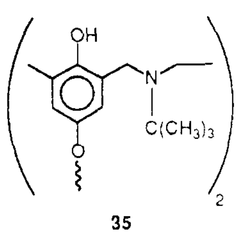

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A similar catalyst at 25 °C produces a polymer containing 529 ppm nitrogen and with a much simpler spectrum. Only a weak resonance at ca. 25 ppm and a very weak one at 96 ppm are observed. At the lower temperature catalyst degradation may have been lessened.

CuBr/DMBA. The reaction is slow with a Cu:DMBA:1 ratio of 1:40:900 at 40 °C but eventually high molecular weight polymer does form. The polymer contains 575 ppm nitrogen and has a complex ^{13}C NMR spec-

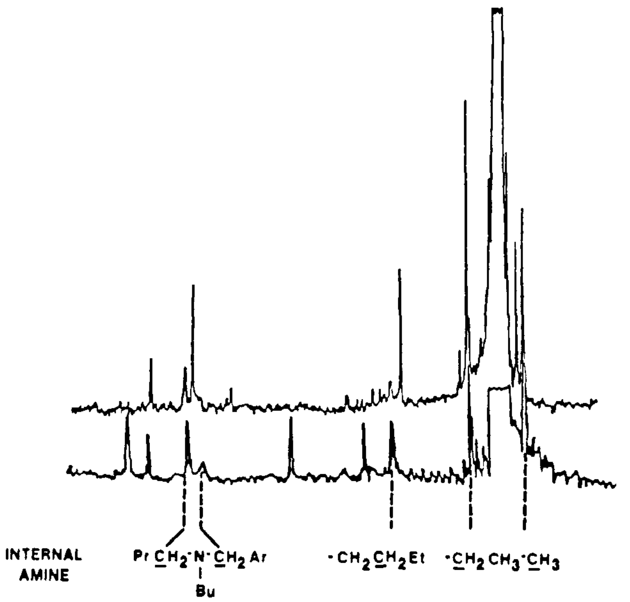


Figure 7. Aliphatic region of the ^{13,}c NMR spectrum of a Cu/DBA PPO before (upper curve) and after (lower curve) heating at 270 °C for 1 min.

trum. A large number of very weak alkyl region resonances are present at 14.6, 20.0, 26.0, 28.1, 29.1, 30.3, 41.0, 49.3, 50.0, 56.9, 94.7, and 101.6 ppm. A dimethylamino and/or a butylmethylamino group and an $ArCH_2N$ group could account for some of these resonances. Amine degradation products appear to have been incorporated. Since DMBA is relatively stable toward oxidation, it would be expected to be degraded to reactive products only during very slow, lengthy polymerizations such as in the example described here.

CuBr/DBED–DMBA. A polymer prepared from a catalyst with a relatively high DBED content (Cu:DBED:DMBA:1 = 1:10:30:900) formed rapidly at 40 °C and contained 920 ppm nitrogen. The ^{13}C NMR spectrum contained only two weak resonances in the aliphatic region (at 26.1 and 95.9 ppm). Amine incorporation is probably related primarily to DBED since DMBA is less reactive than DBED under these oxidative coupling conditions. The spectrum resembles the Cu/DBED reaction described above. At 26.1 ppm resonance may arise from the *tert*-butyl groups of incorporated DBED.

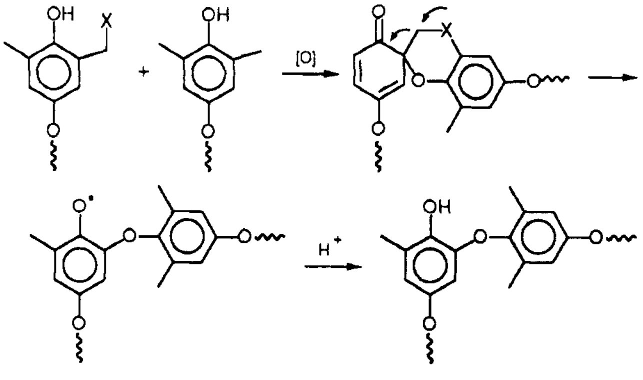
CuCl/TMA–TMEDA. This catalyst[12] produces low nitrogen polymers (40 ppm for the sample described here) and differs from most of the other catalysts by containing only tertiary amines. In the ^{13}C NMR spectrum the trace aliphatic resonances are very weak and occur at 25.7, 29.7, 51.9, 58.1, and 96.2 ppm. As weak as thes resonances are, they are still probably too strong to be due to simple amine degradation products (e.g., incorporated Me_2NH or $MeNRCH_2CH_2NMe_2$) because the values for incorporated nitrogen were so low. Furthermore, dimethylamino groups in the polymer would be expected to have a methyl resonance near 45 ppm (as in DMBA and *N*,*N*-dimethyl-1,3-propanediamine) and not near 52 ppm.

Thermally Treated Polymers. Several of the amine-containing polymers described above were heated at 270 °C for 1 min in a Carver press to simulate the processing conditions that are known to produce a large increase (from 25 to 100%) in the molecular weight of the polymer. The pressed films were dissolved in toluene and then precipitated with methanol to remove any low molecular weight materials that formed during the heating step. The ^{13}C NMR spectra of the heated polymers were very different from the original spectra. All of the resonances assigned to the terminal amino group (i.e., **27**) had disappeared. Resonances assigned to internal amino groups **5a** were retained. Additional, new resonances were seen for some samples but not all of them.

The change in the ^{13}C NMR spectrum in the aliphatic region that a commercial Cu–DBA-type of PPO undergoes on heating at 270 °C is shown in Figure 7. The sample exemplifies the loss of terminal amine, retention of internal amine, and the development of new ^{13}C resonances.

The polymer samples that lose terminal end groups when heated at 270 °C but display almost no other types of anomalous structure (internal amine, etc.) include the Cu/DBED–diethylamine polymer (very weak 94.0 and 96.0 ppm resonances) and the Cu/DBED-*tert*-butylamine polymer (only a weak 29.5 ppm resonance and very weak 96.0 and 103.7 ppm resonances).

The 96 ppm Resonance. A weak resonance at 96 ppm appears in many of the polymers described above. The intensity is normally less than the intensities of tail end groups and sometimes as low as the noise level of the base line. Several possible sources of this resonance are considered here. A resonance in the 96 ppm region could arise from such structures as a 1,3-dioxybenzene, an aryl iodide, or a ketal structure. An aryl iodide is ruled out since no iodides are normally used in the synthesis or found in the polymer by elemental analysis. 1,3-Dioxybenzenes such as **36** could arise during polymerization. Oxidative coupling of an aminomethyl- (or oxymethyl-) terminated chain with an unterminated chain may result in loss of a one carbon fragment by a sequence such as



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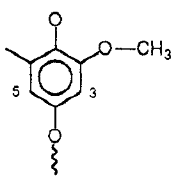
where X is OH, NR_2, etc. Similar reactions involving intermediate cyclohexadienones have been proposed for the oxidative coupling of 2,4,6-mesitol.[33] Two materials with 1,3-dioxybenzene structures that have been selected as models are compound **22** and a PPO copolymer containing 2-methoxy-6-methyl-1,4-phenylene oxide units, **37**. Resonances for the C-3 positions (i.e., for the carbon between the adjacent oxygen-bearing carbons) occur at 99.4 and 98.1 ppm, respectively, for **22** and **37**. Thus, in PPO itself it is possible that a structure such as **36** or the related structure **38** is the source of the 96 ppm resonance.

Ketals, acetals, hemiacetals, etc. also have a resonance near 96 ppm. A ketal such as **39** would be in this class of materials but seems unlikely to be the source of the 96 ppm resonance. Although cyclohexadienone ketals are proposed intermediates in the mechanism of PPO synthesis,[34] such groups are too reactive to exist in the isolated polymer. Furthermore, characteristic carbonyl and olefinic resonances for such a unit are not present



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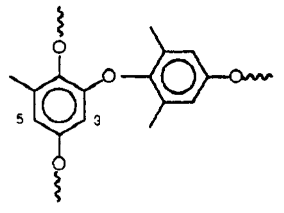

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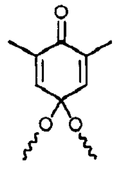

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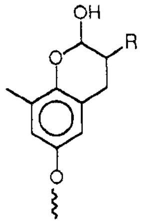
in the NMR spectrum even though some of these resonances should be more intense than the ketal carbon resonance. An end group bearing a hemiacetal unit, however, is a possibility. The likelihood of structure **40** is currently under investigation. These units may arise from coupling reactions of amine degradation products and PPO end groups. Model compounds that contain the cyclic hemiacetal group have chemical shifts of approximately 95 ppm for the resonance of the dioxygenated carbon.[35]



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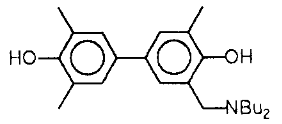
(Aminomethyl)biphenyl Groups. Although the main site of incorporation of a secondary amine onto PPO appears to be at the methyl group of the head end group, it is possible that amino groups could be on biphenyl units too. Diphenoquinone **3** is known to react with DBA to form the aminobiphenol **41**.[22] The reaction requires a solvent such as NMP and normally does not proceed to any significant extent in typical PPO polymerization solvents (e.g., toluene). However, if **41** did arise under oxidative coupling conditions possibly by a different mechanism, it could coredistribute with PPO and be incorporated in the form of the end group **42**. The presence of **42** in PPO probably cannot be distinguished from end group **27** by ^{13}C NMR analysis in the alkyl region, since the (dibutylamino)methyl groups in **41** have almost identical chemical shifts as those in compounds **7** and **8**. The aryl carbon resonances also are expected to be similar to those of end group **26** (e.g., a resonance at 137 ppm) or to be hidden by the strong PPO repeat unit resonances. Even though the amount of **41** cannot be determined by NMR, it is unlikely that **41** is the major amine-bearing unit. Polymers prepared with very little incorporation of **3** (no resonances in the 137 ppm region, which is indicative of the biphenyl moieties **26** and **42**) still have the characteristic resonances of end group **27**.



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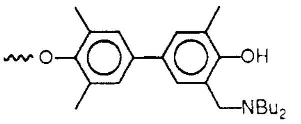

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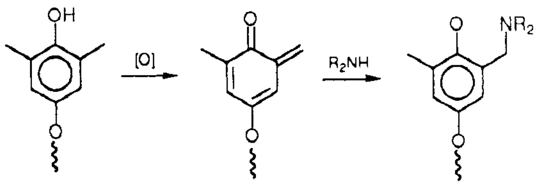
Discussion of Amine Incorporation and Loss. The spectra of PPO samples described above strongly support the presence of amines at the head end positions of the polymer chains. There are a number of routes that could lead to such structures during polymerization. The generation of a quinone methide intermediate **43** may be a key step in many of these routes because quinone methides are known to react rapidly with secondary amines:[36]



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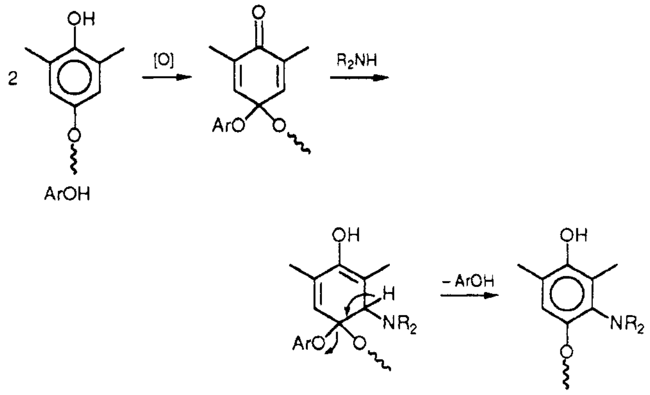
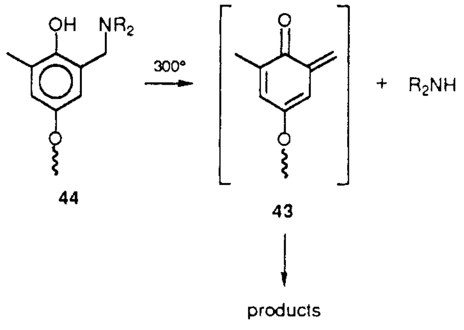
The formation of **43** may occur at a stage in the polymerization when the aryloxy radical concentrations begin to decrease and oxidation of the radical by the catalyst can compete with radical coupling reactions. Another source of **43**, disproportionation of aryloxy radicals, seems less likely since amine incorporation is more prevalent in the later stages of the polymerization reaction when radical concentrations are low. A possible third route to amine incorporation is an oxidative coupling reaction between an amine and an end group while coordinated to the catalyst. Whichever process occurs, the scavenging of amine during polymerization is a very efficient reaction since the amine is incorporated in high conversion even though the concentrations of the amine and the polymer end groups are very low. When the amine is a secondary amine, the corresponding Mannich base phenolic product is the only major amine related product seen by ^{13}C NMR analysis.

Another possible side product during polymerization is 1,4-addition of a secondary amine to a quinone ketal intermediate followed by C–O bond cleavage:



This does not appear to be occurring to an appreciable extent. No characteristic ^{13}C NMR resonances are found for *N,N*-dialkylaniline groups in the polymer that are similar to the shifts in model compounds **21** and **23**.

The loss of the amino end group **27** during processing (250–350 °C) is probably due to the elimination of secondary amine to produce the quinone methide **43**. At the high temperature of processing, the products from



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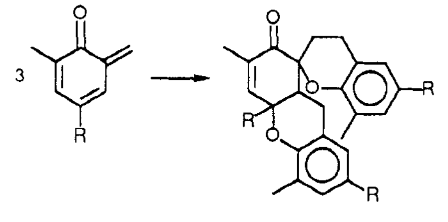
the highly reactive quinone methide will differ from the product formed from 4 during polymerization. Instead of addition of secondary amine to produce **27**, processes such as oxidation of the amine, reduction of the quinone methide, and carbon–carbon coupling of the quinone methide may occur. One type of coupling to be considered is a quinone methide trimerization, which is known to occur at lower temperatures and produce compounds such as **45**.[18,23] A nonreversible addition of the amine to



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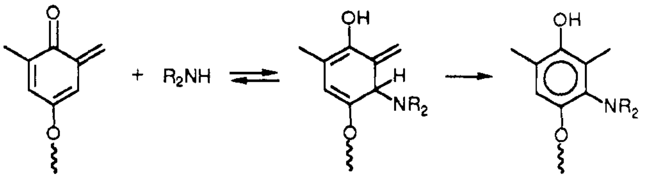
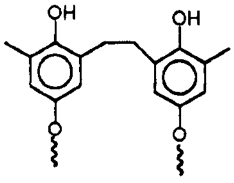
the quinone methide could also occur:



A variety of other coupling processes are possible, such as bridging two chains with an ethylene or methylene group (via units **46** or **47**). No distinctive resonances are found in the processed polymers that are characteristic of these various units (based on analogy with the spectra of compounds **16**–**19**, **22**, **34**, and **45**; R = *t*-Bu). Apparently, a large number of products arise and their concentrations are too low to be detected. Collectively their effects show up in the polymer as increased molecular weight, increased non-H-bonded phenolic hydroxyl absorption, and a decrease in the trace nitrogen content.



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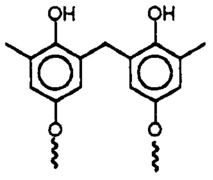

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Registry No. **1** (homopolymer), 25134-01-4; **2** (SRU), 24938-67-8; **6** (homopolymer), 26222-43-5; **6** (SRU), 26545-37-9; **7**, 60460-65-3; **8**, 110861-28-4; **9**, 60460-65-3; **10**, 124462-00-6; **12**, 124462-02-8; **13**, 124462-01-7; **16**, 4397-13-1; **17**, 122109-60-8; **18**, 6538-35-8; **19**, 27179-99-3; **22**, 124462-03-9; **23**, 124481-49-8; **23** amine, 124462-04-0; **43**, 124462-05-1; **45** (trimer), 124462-09-5; TMA, 75-50-3; TMED, 110-18-9; DMBA, 927-62-8; CuBr, 7787-70-4; *N*-bromosuccinimide, 128-08-5; 2-methyl-4-[(dibutylamino)-methyl]phenol, 124462-06-2; 2-methyl-4,6-bis[(dibutylamino)-methyl]phenol, 124462-07-3; manganous chloride, 7773-01-5; benzoin oxime, 441-38-3; *N*,*N*,*N'*,*N'*-tetraethyl-1,2-ethylenediamine, 150-77-6.