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Hydroquinone, Quinone, and Amine Functionalized Polyolefins

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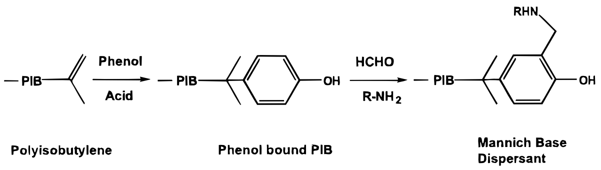
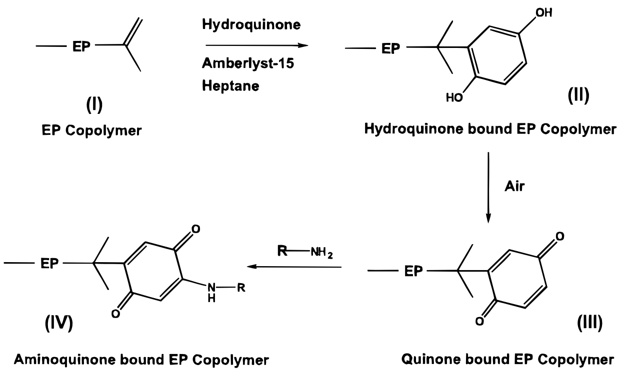
The chemical modification of polymers is of great scientific and technological interest.[1] For example, the modification of polyolefins to impart polar functionality has been pursued for many years. Increased polarity is important for the use of polyolefins in solution (dispersancy) or in solid phase (adhesion, printability). For example, alkylation of phenols by unsaturated hydrocarbons has been studied extensively[2] and these compounds are widely used in the pharmaceutical industry and in petroleum products.[3] Low molecular weight polyisobutylene polymers with one unsaturated double bond per chain have been alkylated with phenol. The phenol-functionalized polymer can be subsequently reacted with amines and formaldehyde to synthesize Mannich base dispersant molecules for lube applications.



In these dispersants, the polyisobutylene chain is responsible for the solubility of the molecule, and the polar amine headgroup keeps the oxidation products and sludge particles suspended in the oil.

In turn, metallocene technology, with its single-site catalysts, has opened up new ways to make polyolefins.[4] Ethylene/α-olefin copolymers produced with metallocene catalysts have narrow compositional and molecular weight distributions. Typically, there is one olefin (especially vinylidene) and one saturated end group per chain. The terminal olefin is produced by chain-transfer reactions involving either β-hydride elimination, β-hydride transfer to ethylene, or metalation followed by rearrangement.[5] Such double bonds could allow a higher level of functionalization in these polymers.



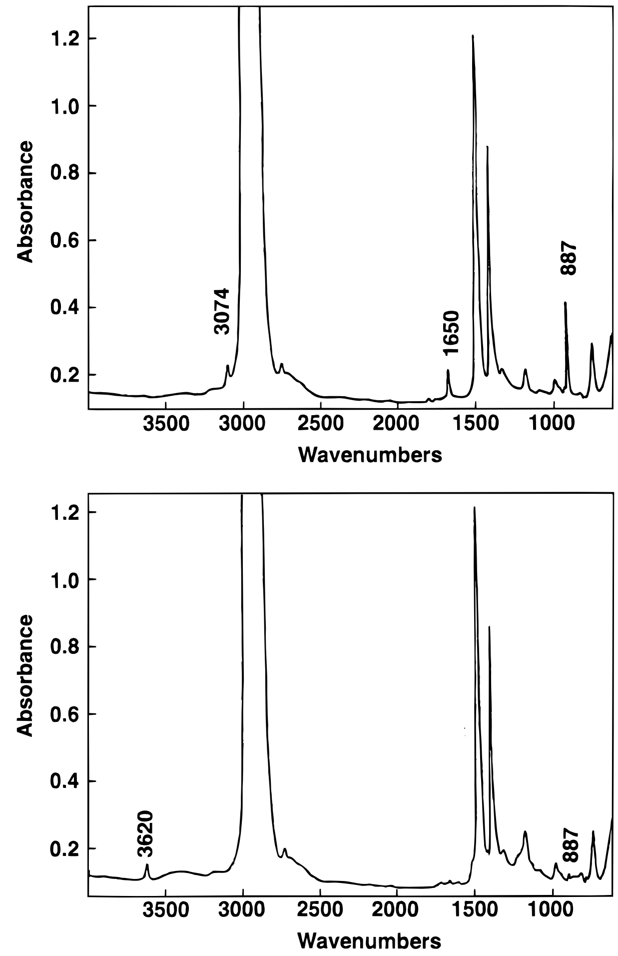


Figure 1. Infrared spectra of the starting EP copolymer (top spectrum) and hydroquinone-reacted EP copolymer product (bottom spectrum).

1-Octadecene has been alkylated with hydroquinone using Amberlyst-15 catalyst.[6] Using a similar alkylation procedure, a low molecular weight ethylene/propylene (EP) copolymer (**I**; M_n 870) with 95% vinylidene terminal double bonds was alkylated with hydroquinone.[7,8] The Fourier transform infrared (FTIR) spectrum of the starting EP copolymer showed double bond absorption peaks at 3074, 1650, and 887 cm^{-1}. These peaks disappeared on alkylation and a new absorption peak appeared at 3620 cm^{-1}, due to hydroquinone grafted EP copolymer (**II**; Figure 1). The ^{13}C NMR spectrum of the starting EP copolymer showed predominantly two types of vinylidene double bonds with peaks at 109.5, 145.7, 111.2, and 144.2 ppm.[5c] The ^{13}C NMR spectrum of the product showed disappearance of all four terminal olefin peaks, and new peaks appeared in the aromatic region (115 to 150 ppm).

Gel permeation chromatography (GPC) of the starting EP copolymer and hydroquinone-alkylated product using refractive index (RI) and ultraviolet (UV) detection are shown in Figure 2. The GPC trace using RI detection is similar both in the starting polymer and the product. The GPC trace using UV detection showed no absorption for the starting EP copolymer. The alkylated product, however, shows UV absorption, suggesting hydroquinone attached to the polymer chain.

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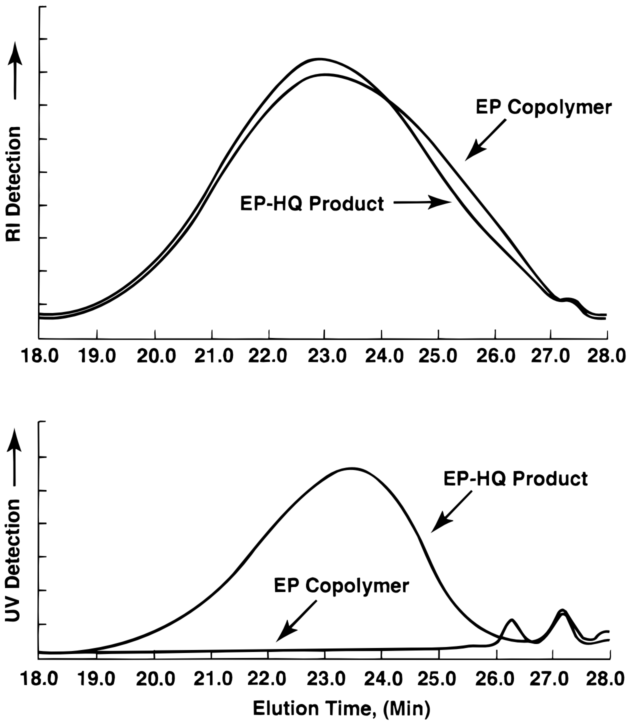


Figure 2. GPC of the starting EP copolymer and hydroquinone-reacted product (top scan: RI detector; bottom scan: UV detector).

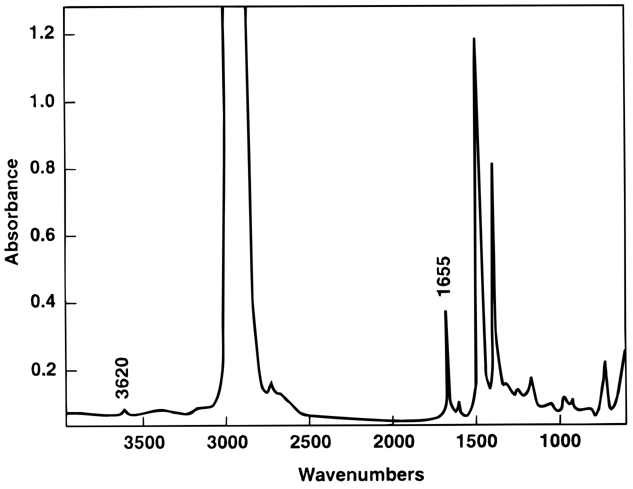


Figure 3. Infrared spectrum of the oxidized ethylene propylene copolymer hydroquinone product.

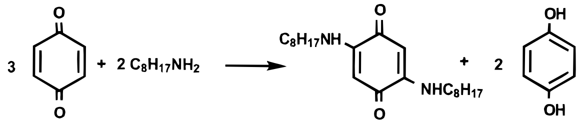
Hydroquinone alkylated with EP copolymer oxidizes to the corresponding quinone form (**III**) even at room temperature. The IR spectrum of the sample stored at room temperature for 1 month showed a decrease in the absorption peak at 3620 cm^{-1} due to the hydroxyl group, and a new carbonyl absorption peak appeared at 1655 cm^{-1}, suggesting substantial conversion of hydroquinone-bound EP copolymer to the corresponding quinone-bound EP copolymer (**III**; Figure 3).

Quinones are known to react with amines under mild conditions to obtain aminoquinones.[9] Quinone-attached EP copolymer was reacted with amine (2:1 mole quinone/amine ratio), such as diethylenetriamine (DETA), to obtain amino-functionalized polymers (**IV**).[11] The IR spectrum of the product showed a broad peak at 3250 cm^{-1} due to amine, along with a carbonyl peak at 1655 cm^{-1}. The product was an effective lube dispersant as measured by the dispersancy bench test.[12]

The technologically important science question for the quinone-amine reaction is whether one can carry the reaction to completion using just 1,4-benzoquinone and 1-octylamine in 1:2 mole ratio, in a such way that the resultant hydroquinone byproduct reoxidizes back to 1,4-benzoquinone with air. Only if the answer to this question is yes, could one use this reaction effectively.

Quinone-Amine Reaction: Model Study

As a model, we have studied the reaction of 1,4-benzoquinone with 1-octylamine at room temperature. In this reaction, 1 mol of 1,4-benzoquinone reacts with 2 mol of 1-octylamine to obtain 1 mol of 2,5-dioctylamino-1,4-benzoquinone product. However, in this process, 2 mol of 1,4-benzoquinone is reduced to form 2 mol of hydroquinone byproduct. To use this reaction effectively, one needs to oxidize the hydroquinone byproduct back to benzoquinone. In earlier studies, calcium hypochloride was chosen as the oxidizing agent despite some issues associated with this reagent.[10]



1,4-Benzoquinone has one carbonyl carbon signal at 186.3 ppm for two equivalent carbonyl carbons, and one signal at 135.5 ppm for the four equivalent double bond carbons. The product spectrum of 2,5-dioctylamino-1,4-benzoquinone shows one carbonyl carbon signal at 178.5 ppm for two equivalent carbonyl carbons. The double bond peaks, however, are split into two separate resonances. The signal at 151.8 ppm is due to the carbon with the alkylamine group attached, and the response at 93.1 ppm is due to the carbon with one hydrogen attached (from couple spectra). The ^{13}C NMR resonance at 42.2 ppm, which is due to the C1 carbon of the 1-octylamine in the starting amine, moves to 43.1 ppm in the product. Thus, ^{13}C NMR can be conveniently used to follow this reaction with respect to all reagent disappearance and product formation.

To follow the course of the reaction, we ran the reaction in a NMR tube using 1:2 mole ratio of 1,4-benzoquinone and 1-octylamine in benzene solvent. The ^{13}C NMR spectrum shown in Figure 4 (#1) is the reaction mixture after 15 min. As shown in the figure, all benzoquinone carbonyl carbon peaks at 186.3 ppm and the signal at 135.5 ppm (representing the four double bond carbons) have completely disappeared and a new carbonyl peak due to the disubstituted product at 178.5 ppm and the peaks at 151.8 and 93.1 ppm due to the double bond carbon appeared. There is no sign of monoadduct formation because that product would have two separate carbonyl carbon signals. There are, however, peaks due to unreacted 1-octylamine that are present, along with the product peaks, suggesting the presence of substantial unreacted octylamine in the mixture. The ^{13}C NMR spectrum also shows two resonances at 151.4 ppm due to aromatic carbons (with two equivalent hydroxyl groups) and at 117.2 ppm (due to four equivalent aromatic carbons). These results indicate formation of 1,4-hydroquinone as a byproduct in the reaction. The reaction mixture also shows several small signals, especially in the double bond and carbonyl regions.

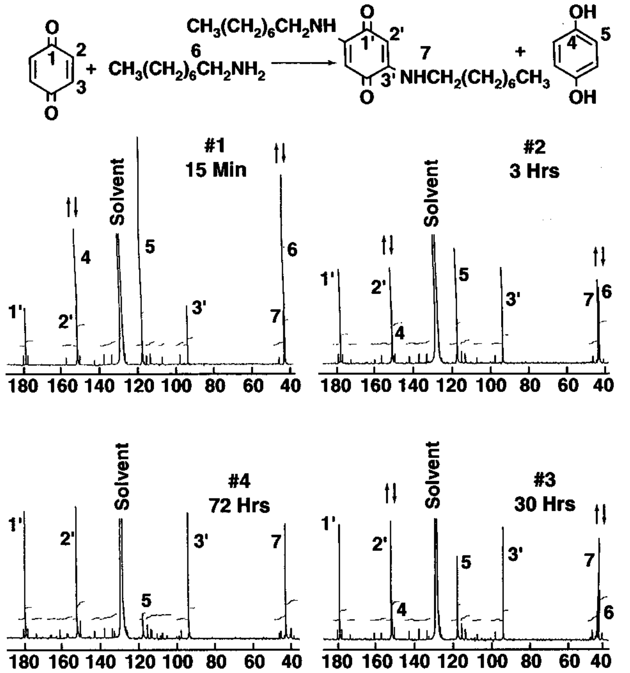


Figure 4. ^{13}C NMR spectrum of the reaction mixture of 1,4-benzoquinone, 1- octylamine after 15 min (#1), 3 h (#2), 30 h (#3), and 72 h (#4).

The ^{13}C NMR spectrum of the reaction mixture after 3 h is shown in Figure 4 (#2). The spectrum is very similar to the one shown in Figure 4 (#1), except relative hydroquinone peaks and carbon next to amine of 1-octylamine are diminishing in intensity, and the product resonances are increasing in intensity. The ^{13}C NMR spectrum of the reaction mixture after 30 h is shown in Figure 4 (#3). Again, the spectrum is very similar to the one before, except the relative hydroquinone resonances and C1 carbon next to the amine of 1-octylamine have disappeared and the product peaks are increasing. The ^{13}C NMR spectra of the reaction mixture after 72 h is shown in Figure 4 (#4). The ^{13}C NMR spectrum of the reaction mixture after 72 h is very similar to that of the pure product. Thus, one can obtain the desired product, 2,5-dioctylamino-1,4-benzoquinone, in high yields using just 1:2 mole ratio of the reactants 1,4-benzoquinone and octylamine, using air as an oxidizing agent.

Conclusion

Mannich base dispersants are an important class of lubricant additives. These additives typically are prepared by reaction of low molecular weight polyisobutylene alkylated phenols with amines and formaldehyde. In contrast, we have alkylated low molecular weight EP copolymers with terminal double bonds with hydroquinone. These hydroquinone alkylated polymers were oxidized to their corresponding quinone form. We have shown that, 1,4-benzoquinone can react with 1-octylamine at room temperature using a 1:2 mole ratio, in a such way that the resultant hydroquinone byproduct reoxidizes back to 1,4-benzoquinone with air. Unlike Mannich base lube dispersants, the quinone bound EP copolymers were directly reacted with amines, *without formaldehyde*, to obtain novel functionalized polymers for lube applications.

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References and Notes

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(8) A typical example of the hydroquinone alkylation of EP copolymer is shown as follows: To a 250-mL round-bottomed flask equipped with water condenser, a dropping funnel was charged with 6.32 g (0.057 mol) of hydroquinone, 15 g of Amberlyst-15 (0.0705 mol/equiv) and 50 mL of heptane. [Amberlyst-15: registry no. 39389-20-3; benzenesulfonic acid, ethenyl-, polymer with diethenylbenzene has a formula $(C_{10}H_{10}\cdot C_8H_8O_3S)_x$, possesses high acidity (4.7 meq/g), high porosity (32%), and high surface area (45 m^2/g). (Martella, D. J.; Jaruzelski, J. J.; Chen, F. J. U.S. Patent 5,262,508. 1993.] The mixture was heated to 98 °C and stirred under nitrogen. A 50-g quantity of EP copolymer (M_n 870, 0.057 mol) with 95% vinylidene terminal double bonds was then added showly to the aforementioned solution, and the mixture was refluxed for 6 h under nitrogen. The reaction mixture was then filtered, and the filtrate was evaporated on rotary evaporator to obtain the product.

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(11) Alkylated quinone adduct (2 g, 2×10^{-3} mol) was dissolved in 50 mL of heptane, and 0.103 g (1×10^{-3} mol) of diethylenetriamine (DETA) was added. The solution was stirred at room temperature for 72 h. The product was diluted with 50 mL of heptane and filtered. The solvent was removed initially by nitrogen stripping and then by high vacuum.

(12) Patil, A. O. U.S. Patent 5,576,274, November 19, 1996.

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