

HYDROQUINONE COPOLYMERS: MODELS FOR RETROGRADE REACTIONS IN LIQUEFACTION PROCESSING

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The identification of structures responsible for retrograde reactions is a high priority research objective in coal liquefaction. Interest has focused on the cleavage of benzyl aryl ethers and subsequent polymerization of the fragments. In our work, the reactions of the polyethers prepared by reaction of bis(bromomethyl)naphthalene with hydroquinone were investigated in a tetralin system. Analysis of the products from the copolymers demonstrated that almost all of the naphthyl moieties were converted to dimethylnaphthalene, whereas the hydroquinone groups were converted to very high molecular weight macromolecules. Light-scattering studies showed that the product has a very high depolarization ratio, a property also demonstrated by coal macromolecules obtained by mild liquefaction and extraction but not by synthetic polymers, including polyphenylene oxides. Similar macromolecules were obtained in thermal reactions of benzyloxyphenol and dihydroxybenzenes in tetralin.

Key words: benzyl aryl ether cleavage, retrogressive reactions, dihydroxybenzene polymers

INTRODUCTION

Formation of char during coal liquefaction is deleterious to the process because of deposition on the catalyst as well as in the apparatus. Phenolic groups have been implicated in the retrogressive reactions that result in char formation in SRC materials (1,2); however, the nature of the condensation reaction that the phenolic substances undergo has never been precisely defined. The addition of hydrogen donors, such as tetralin, to SRC fractions with high phenolic content inhibited char formation (2). It is important to note in these studies that derivatization of the phenolic groups in the SRC with acetic anhydride resulted in higher char yields when the acetylated products were heated. The explanation for this was that the thermally labile esters readily decomposed forming phenoxy and acetyl radicals, which then abstracted hydrogen from other coal groups. Dimerization and addition reactions of the resulting radicals would result in char formation.

The thermal reactions of benzyl phenyl ether have been investigated as a model for the cleavage of the oxymethylene bridge in coal. The data from these modeling experiments is consistent with a mechanism involving homolytic cleavage of the C-O bond, forming phenoxy and benzyl radical intermediates. In a good hydrogen donor solvent such as tetrahydroquinoline, the radicals are capped and toluene and phenol are formed (3). However, when hydrogen donor solvent was not present or even in the presence of some tetralin, addition or condensation products were obtained (4).

The presence of dihydroxyarenes in coal structures and the well-known tendency of dihydroxybenzene to condense to polymers under oxidative conditions (5) suggests that retrogressive reactions of compounds containing dihydroxy or dioxy groups should be investigated under conditions typical of coal liquefaction. The initial model chosen for this investigation was the insoluble copolymer, poly(2,6-dimethylnaphthaleno-1,2-dioxybenzene). The 1,4-substituted analog was previously used in modeling coal pyrolysis and swelling studies (6,7,8). Reactions of the

copolymer and related monomers were carried out in tetralin so that we could determine whether retrogressive reactions could occur even when hydrogen donor solvent molecules are readily available.

EXPERIMENTAL

The procedure of Squires et al. (6) was used for preparation of poly(2,6-dimethylnaphthaleno-1,4-dioxybenzene). 1,2,3,4-Tetrahydronaphthalene (tetralin), hydroquinone, catechol, and 4-benzyloxyphenol were obtained from Aldrich.

The reactions were carried out in a 75-ml stainless steel reactor. The reaction vessel was charged with 2.00 g of model compound or polymer and 16 g of tetralin, evacuated, sealed, and heated in a fluidized sand bath at 420°C for 6 min with shaking. The tube was removed from the sand bath, cooled, slowly depressurized and opened. The product slurry was transferred into a centrifugation bottle by washing with hexane, and the solid product was removed by centrifugation. The hexane-soluble product was analyzed by GC/FTIR/MS.

The hexane-insoluble product was separated into tetrahydrofuran (THF)-soluble and insoluble fractions by extraction of the solid into that solvent. The THF-soluble product was sublimed at 110°C/1.2 torr for two hrs. The sublimate was analyzed by GC/FTIR/MS. The residue left after sublimation was analyzed by FTIR and ¹³C NMR in THF-d₆. Molecular weight determinations were performed by GPC and low-angle laser light scattering photometry. The THF-insoluble fraction was analyzed by FTIR.

RESULTS AND DISCUSSION

The thermal reaction of the mixture of poly(2,6-dimethylnaphthaleno-1,4-dioxybenzene) in tetralin at 420°C for 6 min resulted in extensive degradation of the copolymer. The product distribution was 6.5% THF-insoluble material, 28% hexane-insoluble, THF-soluble fraction, and 63% hexane-soluble fraction. The hexane-soluble fraction consisted mostly of dimethylnaphthalene and a small amount of solvent-derived dimers. Since the weight % composition of dimethylnaphthalene units in the copolymer is 60%, the formation of dimethylnaphthalene was nearly stoichiometric.

The THF-soluble fraction was sublimed under vacuum (110°C, 1.2 torr) to remove low molecular weight material. A small amount of hydroquinone was isolated as the sublimate. The majority of the fraction did not volatilize. The residue from vacuum sublimation was redissolved in THF, and the molecular weight was determined by low-angle laser light scattering photometry with Cabbanes factor corrections (9). Depolarization ratios were large for the set of solutions, resulting in Cabbanes factors as large as 3.61 for a 0.13 mg/ml solution. These high depolarization ratios are comparable with those obtained for coal macromolecules, which also scatter light anisotropically. Most synthetic polymers, including poly(phenylene oxide), have low depolarization ratios. The reciprocal Rayleigh plot of the Cabbanes-corrected scattering factors was nearly linear ($r^2 = .97$) with a positive slope ($A_2 = .0063$). The weight average molecular weight (M_w) was 1.92 million Da.

The high yield of dimethylnaphthalene indicates that the predominant pathway involves cleavage of the C-O (benzyl ether type) bonds. The resulting naphthylmethylene radicals are presumably rapidly capped by the hydrogen donor solvent. The fate of the oxy radical in this reaction is different than that of the phenoxy radical produced in the benzyl phenyl ether reaction. Only a portion of the oxy radicals produced from cleavage of the ether groups in the copolymer were converted to hydroquinone, while the majority were condensed to a high molecular weight material.

To further elucidate the difference between the mono and dioxybenzene systems, the thermal reaction of 4-benzyloxyphenol was carried out in tetralin under the same conditions. This model compound represents a single unit of the copolymer and was expected to give toluene from the benzyl radical as well as the reaction products from the oxyphenol radical. This reaction produced the expected toluene, the THF-insoluble fraction, and the hexane-insoluble, THF-soluble fraction. However, the amount of the THF-soluble fraction was smaller (14%) than that obtained from the copolymer. Sublimation of this fraction gave a small amount of hydroquinone. The molecular weight of the sublimation residue was 3.14 million Da. Depolarization ratios were similar to those observed for the product from the thermal reaction of the model polymer, resulting in Cabannes factors of 4.77 for the 0.12 mg/ml solution. The reaction of 4-benzyloxyphenol in tetralin has been reported previously (10), but no details concerning the product were given. The thermal reaction of methoxyphenols in tetralin were studied by Bredenbergh and Ceylon (11). The yields of hydroquinone from 4-methoxyphenol were quite small, but the fate of the oxy radicals generated from this ether were not elucidated, since polymeric materials were not investigated. Similar poor recoveries of products from tetralin reactions of hydroquinone and 4-methoxyphenol were mentioned by Kamiya et al. (12).

The thermal reactions of dihydroxybenzenes in tetralin were reinvestigated to determine the nature of the products and their similarity to those from the ether reactions. The reaction of hydroquinone in tetralin at 420°C was carried out, and a hexane insoluble, THF soluble fraction containing the anisotropic polymeric product ($M_w = 0.95$ million Da) was obtained. Thus the cleavage of the phenolic O-H bond may give an oxyphenol radical which may be the same species as that produced in the ether C-O cleavage discussed above.

Catechol was also heated in tetralin at 420°C. Again, a polymeric product ($M_w = 1.97$ million) was obtained. The polymer from the catechol was also anisotropic, giving a Cabannes factor of 3.63 for the 0.14 mg/ml solution.

Infrared spectra of the THF-soluble polymers exhibit large broad hydroxyl stretching absorptions similar to coals. Bands characteristic of both phenols and aryl ethers occur at about 1200 and 1260 cm^{-1} , respectively. A small band corresponding to conjugated carbonyl is present at 1700 cm^{-1} . In addition to the aromatic C-H stretching bands, aliphatic bands are also present, probably from incorporation of tetralin into the polymer. Cronauer has previously discussed the tendency of radicals to incorporate tetralin (13). Further characterization of the polymeric materials is in progress.

Schlosberg et al. (4) have described a number of potential reactions of the benzyl and phenoxy radicals that result from homolytic cleavage of benzyl phenyl ethers. Most of these will also apply to oxy radicals produced in the cleavage in the dioxy systems. Until detailed information on the structures in the polymers is available, we obviously can not write detailed mechanisms for the polymer formation. We can, however, state the following generalizations:

- (1) The oxy radicals are more involved in the polymer formation than the naphthylmethylene or benzyl radicals produced in the homolytic C-O cleavage reactions of ethers of dihydroxybenzenes. This is shown by the recovery of most of the dimethylnaphthalene units as dimethylnaphthalene and benzyl as toluene. This contrasts with the reactivities of phenoxy versus benzyl radicals, which were approximately equal in the presence of hydrogen donor solvents (4).
- (2) The thermal reactions of dihydroxybenzenes and their ethers in tetralin result in polymeric products in contrast with the reactions of phenyl ethers that give additional by-products composed of mainly two or three rings (4,14).

The oxygen functional groups in coals undoubtedly play an important role in coal liquefaction. Although benzyl phenyl ether linkages are cleaved under relatively mild liquefaction conditions, we see from this study that some of the radicals resulting from this scission may readily condense into highly anisotropic macromolecules, even in the presence of hydrogen donor solvents.

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