

Controlled molecular weight cresol–formaldehyde oligomers

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Abstract

Controlled molecular weight, linear, *ortho*- and *para*-cresol novolac oligomers have been synthesized by using calculated amounts of a monofunctional 2,6-dimethylphenol endcapping reagent. It was found that an excess of formaldehyde was needed to achieve the targeted molecular weights, thus suggesting that a dynamic equilibrium exists in these reactions whereby formaldehyde adds and eliminates from the cresol rings. Reaction progression was monitored by both ^{13}C NMR and GPC. Number average molecular weights of these oligomers were confirmed using ^{13}C NMR spectra and were found to be comparable to the targeted molecular weights.

The glass transitions and viscosities of both the *ortho*- and *para*-cresol novolacs were compared at equivalent number average molecular weights. The T_g s increased as the molecular weights increased, but there were no observable differences between the T_g s of *ortho*- and *para*-cresol novolacs with similar molecular weights. The melt viscosities of *ortho*- and *para*-cresol novolacs with similar molecular weights were almost identical. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

Phenolic resins are among the oldest known and highest volume thermosetting materials produced in the United States [1]. Among the numerous attractive properties of phenolic resins and their networks are low cost and excellent flame retardance [2,3]. Therefore, we and others are investigating this class of materials as possible matrix resins for flame retardant structural composites. The most common phenolic pre-polymers are derived from reacting phenol with formaldehyde or with formaldehyde derivatives. This reaction occurs most rapidly under extremely acidic or basic conditions. The pH of the reactions and the stoichiometric ratio of the monomers give rise to two classes of phenolic pre-polymers known as novolacs and resoles.

Novolac oligomers are prepared in acidic media using an excess of phenol over formaldehyde. The mechanism associated with this reaction has been described in four steps (Fig. 1). First a methylene glycol is protonated by an acid from the reaction medium, which then releases water to form a hydroxymethylene carbonium ion (step 1). This ion acts as a hydroxyalkylating agent by reacting with a phenol via electrophilic aromatic substitution. A pair of

electrons from the benzene ring attacks the electrophile forming a carbocation intermediate followed by deprotonation and regain of aromaticity (step 2). The methylol group of the hydroxymethylated phenol is unstable under acidic conditions and loses water readily to form a benzylic carbonium ion (step 3). This ion then reacts with another phenol to form a methylene bridge in another electrophilic aromatic substitution. This major process repeats until the formaldehyde is exhausted [4].

Typically 0.75–0.85 mol of formaldehyde are used for each mole of phenol in the synthesis of low molecular weight novolacs [1], and branched oligomers with phenol endgroups are formed since phenol is used in excess. These pre-polymers are thermally stable and can be stored effectively. Novolac crosslinking is usually achieved by introducing a source of methylene groups to form additional methylene bridges between aromatic rings. Hexamethylenetetramine (HMTA) is the most widely used curing agent (source of formaldehyde) for these reactions. Other curing agents with limited importance include *para*-formaldehyde and trioxane [1].

Resoles are obtained by reacting an excess of formaldehyde with phenol under basic conditions. This produces resins with aromatic methylol groups derived from the excess of formaldehyde. Resoles are fairly stable at ambient temperatures, but react rapidly at elevated temperatures forming methylene linkages by eliminating water and

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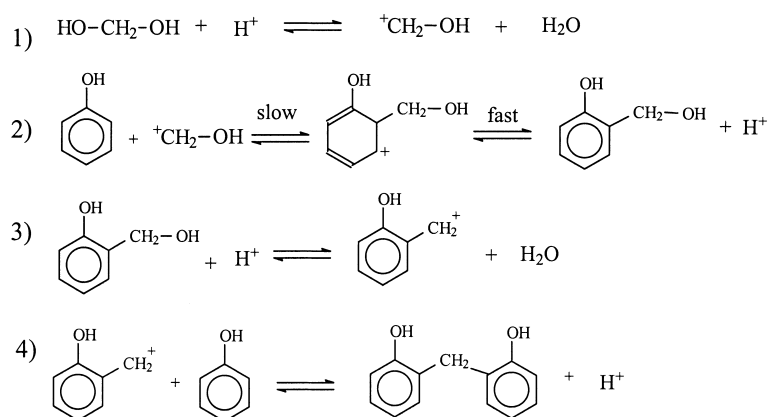


Fig. 1. Mechanism for the major process of phenolic novolac resin synthesis.

other by-products. Since these materials can be ‘self’-cross-linked thermally, long-term storage is more difficult.

Regardless of the curing method, either by introducing a crosslinking agent or by thermal self-condensation, the network forming process is accompanied by the generation of volatile by-products such as ammonia, water and formaldehyde. Volatiles often cause voids in the networks [5–7]. This, along with a lack of control over crosslink density, results in brittle networks.

Void-free networks can be prepared by reacting phenolic novolacs with epoxies in reactions where the phenolic hydroxyl groups react with the epoxy groups [8–11].

Workers in our laboratories have previously demonstrated that phenolic–epoxy networks with high phenolic compositions, and with a relatively high phenol functionality per chain (~7), exhibit significantly improved toughness while retaining most of the flame retardant properties [12,13]. These improved mechanical properties were correlated with increased molecular weights between crosslinks achieved by leaving many phenolic hydroxyl groups unreacted.

Linear, cresol novolac oligomers, obtained by reacting difunctional *ortho*- or *para*-cresol with formaldehyde, are widely used as coatings, adhesives, electronic insulation materials, and for automotive applications [1]. Low molecular weight oligomers have also been reacted with epichlorohydrin to form epoxy resins [8]. A *para*-cresol novolac ($M_n = 580$ g/mol) exhibited a semi-crystalline structure with good thermal stability [14]. *Ortho*- and *para*-cresol have also been copolymerized with *meta*-cresol for use in the electronic industry as photoresists. Since *ortho*- and *para*-cresol have slower reaction rates with formaldehyde than *meta*-cresol, oligomers with *meta*-cresol blocks were obtained having primarily *ortho*- or *para*-cresol endgroups [15,16].

Ortho- or *para*-cresol novolac formation, which involves exclusively difunctional monomers, are linear condensation polymerizations. The molecular weights of these cresol novolacs, therefore, should depend on the monomer feed ratio. However, to date, cresol resin syntheses follow typical

phenolic novolac synthesis procedures where reactions are terminated at a pre-determined viscosity or reaction time. The difficulty in molecular weight control arises from side reactions, which offset the stoichiometric ratio necessary to obtain target molecular weights. This paper describes the synthesis of linear controlled molecular weight cresol novolacs. The degree of molecular weight control achievable and properties such as glass transition temperatures, molecular weight distributions, and melt viscosities will be discussed. These cresol novolacs have also been cross-linked with epoxies. The network formation reactions and their properties will be addressed in a separate paper.

2. Experimental

2.1. Materials

Ortho-cresol (99 + %), *para*-cresol (99%), 2,6-dimethylphenol (99%), *para*-formaldehyde (powder, 95%), formaldehyde (37 wt% solution in water), and oxalic acid dihydrate (99%) were obtained from Aldrich. A commercial phenolic resin was kindly provided by Georgia-Pacific (Product #GP-2073). All reagents were used as received.

2.2. Molecular weight calculations

The following method was used to calculate the stoichiometric ratio of monomers required to obtain specified number average molecular weights. The molecular weight of two endcapping molecules, 2,6-dimethylphenol, and one methylene linkage, $-\text{CH}_2-$, were subtracted from the total targeted molecular weight. The remaining weight was divided by the molecular weight of each repeat unit (120 g/mol) to obtain the number of repeat units within the chain (x). The stoichiometric ratio then consisted of two moles of 2,6-dimethylphenol, x moles of cresol, and $x + 1$ moles of formaldehyde. The following example is for the stoichiometric calculation of reactants for a 2000 g/mol oligomer capped on each end with 2,6-dimethylphenol. The combined molecular weight of the

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