

Synthesis and Characterization of Lactose Based Resorcinol Resin

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ABSTRACT: Resorcinol-lactose resin was synthesized using phosphoric acid as the catalyst at 95°C. ¹³C-NMR measurements proved that the chemical reaction is initiated at the 4- or 6-carbon position in benzene ring. Sample separation by size-exclusion chromatography (SEC) technology indicated that the resin consists of reacting mixtures of oligomer of lactose, glucose, and galactose with resorcinol. The

resin, using a by product of dairy industry as a main component, could be potentially applied as a novel adhesive to the wood process industry. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2581–2585, 2002

Key words: resorcinol-lactose resin; ¹³C-NMR, size exclusion chromatography

INTRODUCTION

Lactose is a reduced sugar, because, under acid or base condition, its β -D-galactopyranosyl- α -D-glucopyranose structure is in equilibrium with a small amount of open-chain aldehyde isomer.¹ Thus, lactose can be potentially used to react with phenols for making phenolic resins. Lactose-based phenolic resins are not only environmental friendly, as it eliminated the formaldehyde component in the products, but also may help to challenge a serious disposal problem in the dairy industry where large amounts of cheese whey, mostly lactose, were produced.

Syntheses of lactose-based phenolic resins have reported by Tito and co-workers.² They used whey permeate to react with phenol under the acid condition for making thermosetting resins. These resins can be used to prepare high-density thin particle boards that exhibit good strength and water resistance. However, high temperature and pressure for curing prevented it from being employed as a suitable plywood adhesive. Later, they synthesized lactose-modified phenol-formaldehyde resin under an alkaline condition.³ The results showed that lactose/whey permeate and lactose derivatives can be used to modify phenol-formaldehyde resin that exhibits good water resistance after being cured.

In this work, we report the synthesis of another lactose-based phenolic resin using resorcinol. As is known, the reactivity of resorcinol with aldehyde is greatly increased by introduction of a second hydroxyl group into the phenol nucleus, usually 12 times faster than that of phenol.⁴ Also, its resins possess high bonding strength, creep resistance, resistance to high humidity and water, and excellent long-term durability.⁵ Unfortunately, only a few studies on resorcinol reacting with monosaccharide and disaccharide, such as glucose⁶ and cellobiose,⁷ have been reported. Presently, we used α -lactose-monohydrate to react with resorcinol using phosphoric acid as the catalyst. The reaction mechanism, possible molecular structure as well as the influence of the mol ratio of monomers and catalyst on the final products have been exploited.

EXPERIMENTAL

Materials

α -Lactose-monohydrate and resorcinol were purchased from Aldrich and used as received without any further purification. Phosphoric acid is 85% standard purity from Allied Chemical Company.

Synthesis

Synthesis of resorcinol/lactose (R/L) resins was followed the conventional procedure of novolak's. Different mol ratios of resorcinol/lactose/phosphoric acid were used to study its effect on the final products. Specifically, 9.8 g of lactose and 2.8 g of resorcinol and

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TABLE I
Recipe and Reaction Condition for Resorcinol/Lactose Resin

Sample	Lactose (g)	Resorcinol (g)	Phosphoric Acid (g)	Reaction Temperature °C	Reaction Time Hour
A	9.8	6	6	95	2
B	9.8	2.8	6	95	2
C	9.8	1.4	6	95	2
D	9.8	2.8	4.2	95	2
E	9.8	2.8	1.5	95	2

5 mL of water were added into a 250 mL three-necked flask, equipped with a mechanical stirrer. After stirring for about 5 min, 3.9 mL of phosphoric acid was added into the slurry. The temperature, then, was increased gradually to 95°C. By this time, the slurry became a yellowish transparent solution. Having kept the reaction about 1 h, the system was attached to a vacuum for removing water. When the viscosity of the solution increased greatly, and the resin appeared red-dish, the reaction was stopped. The product was removed to a glass container for further analysis. The recipe of samples with a different mol ratio of lactose and resorcinol was shown in Table I.

¹³C-NMR measurement

¹³C-NMR spectra were obtained on a QE-300 spectrometer, operating at 75 MHz. DO₂ was used as the solvent.

Size-exclusion chromatography (SEC) experiment

Resins synthesized were conducted in the separation experiment by SEC, with a Toyopearl HW-40F column, and using deionized water as the mobile phase. The exclusion limit of the column was 3000 ± 30% Daltons. The rate of elution was 0.303 mL/min, and the sample concentration was 0.8% in deionized water.

RESULT AND DISCUSSION

The reaction mechanism of lactose-based resorcinol resin

¹³C-NMR spectra of resorcinol, lactose, and R/L resin (sample C) are shown in Figure 1. It is evident that, in addition to original chemical shifts of carbons from pure resorcinol and lactose,^{8,9} several new chemical shifts appear around at 63, 92, 96, 120, and 153 ppm in the spectrum of R/L resin, respectively. Furthermore, the peak features show some broadening effect compared with the spectra of pure monomers.

Theoretically, when free aldehyde groups of lactose react with resorcinol, the electrophilic substitution reaction in the benzene ring may mostly occur at the 4-

or 6-carbon position due to the powerful activation effect of the hydroxyl groups at 1,3 carbon position in resorcinol.¹ As in Figure 1, a prominent new peak, which emerges at 120 ppm in the spectrum of R/L resin, and can be assigned as the reacted carbon at the 6-position in resorcinol, strongly suggests these condensation reactions indeed took place.¹⁰ Another evidence, which can support this mechanism, is from a chemical shift at 107 ppm. A strong peak being originally from the 4- and 6-carbon position in resorcinol⁴ reduces into a smaller peak, indicating some alteration of chemical environment in both carbons. Furthermore, a smaller peak appears at 153 ppm. This reflects the influence of substitution reaction at the 4- or 6-carbon position on the 1- or 3-carbon in the benzene

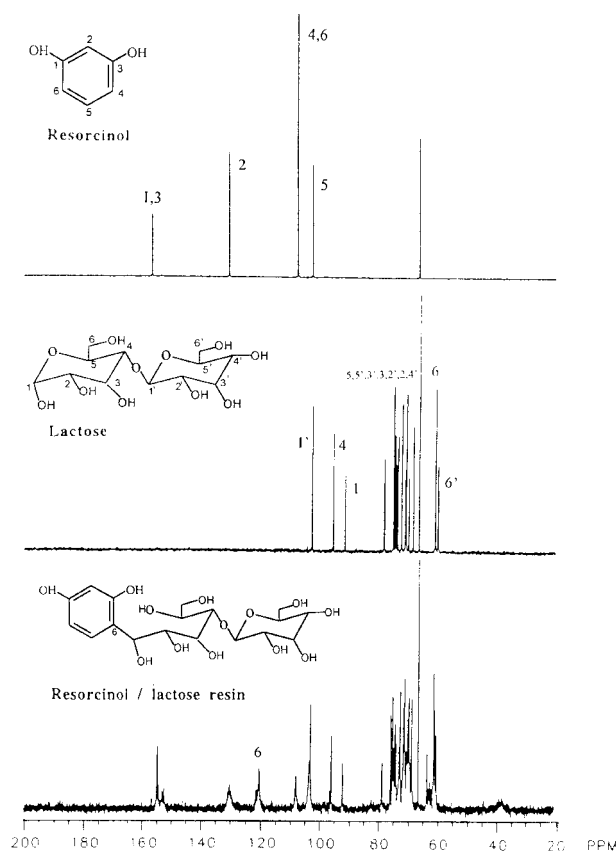


Figure 1 ¹³C-NMR spectra of resorcinol and lactose, resorcinol/lactose resin of sample C at 75 MHz in DO₂.

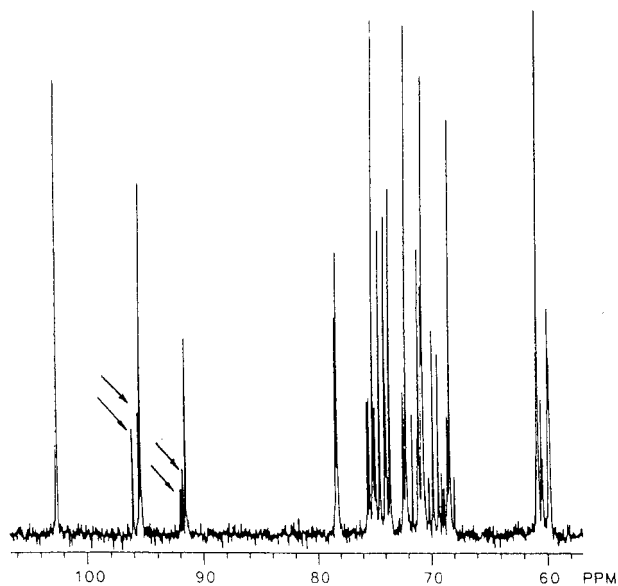


Figure 2 ^{13}C -NMR spectrum of lactose, after subjecting hydrolysis by phosphoric acid, at 75 MHz in DO_2 .

ring.¹¹ Also several new chemical shifts occur at 63, 92, and 96 ppm. These peaks may be attributed to glucose and galactose compounds,¹² which are products of the hydrolysis of lactose under the acid condition. For precisely identifying them, we have tried the same recipe without adding resorcinol under the same reaction condition. In this case, the sample filtration is needed for NMR measurement, because lactose can only be partially dissolved into phosphoric acid. Figure 2 presents the NMR spectrum of lactose heated with phosphoric acid at 95°C for 1 h. It is found that four new chemical shifts occur around 92 and 96 ppm. Compared to the lactose's ^{13}C -NMR spectrum in Figure 1, these chemical shifts (arrow's pointing in Fig. 2) confirm the existence of α - and β -isomers of glucose and galactose.¹² Thus, as both glucose and galactose are reduced sugar, it is reasonable to assume that lactose-based resorcinol resin is a reaction mixture of resorcinol with lactose, glucose, and galactose.

The molecular structure of lactose-based resorcinol resin

To study the chemical reaction mechanism and the influence of the monomer ratio and reaction conditions on final products, sample separation experiments were performed using size-exclusion chromatography (SEC). To identify the pure compounds including glucose, Figure 3 presents the separation result of two simple mixtures of resorcinol with lactose and glucose at room temperature. It is evident that the separation effect in both cases is fairly good. As the molecular weight of lactose is larger than that of glucose, the retention time for lactose is 1.3 h and for glucose is 1.5 h. For resorcinol, in both cases, the

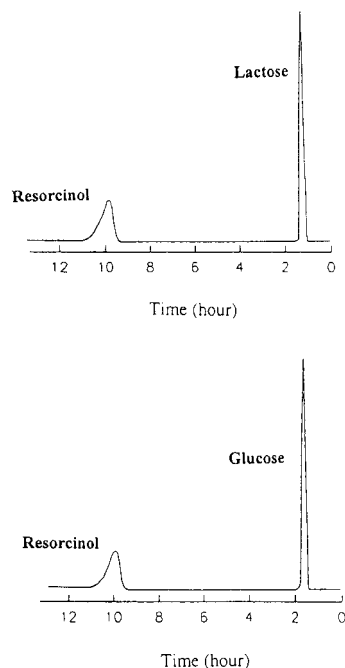


Figure 3 SEC spectra of two mixtures of resorcinol with lactose and glucose.

retention time is exactly 10 h. Based on these data, the SEC results of R/L resins with different resorcinol content are shown in Figure 4. First, compared with

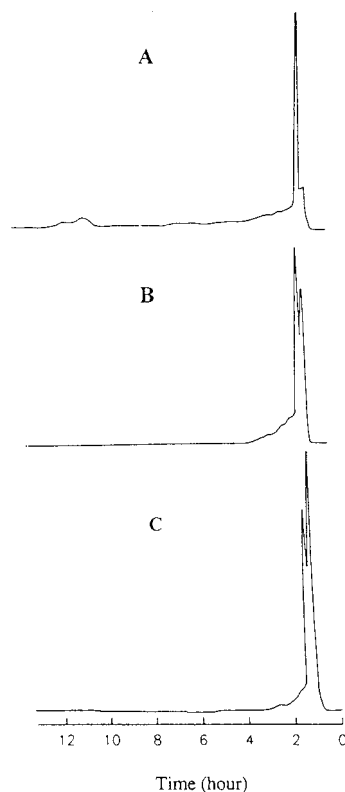


Figure 4 SEC spectra of resorcinol/lactose resins synthesized with different content of resorcinol.

pure lactose, the retention time of the first peak of R/L resins for all samples is around 1.0 h. The retention time is evidently reduced, indicating the product contains the component with a larger molecular size. However, as the retention time is not changed greatly, it suggests that the molecular weight of R/L resins may be still relatively low. Combined with the NMR data, we find that R/L resins consist of a series of different molecular sizes with mainly lactose, glucose, and galactose condensing with resorcinol.

In accordance with SEC's separation mechanism, the double peaks for sample A, B, C in Figure 4 also suggest that R/L resins may consist of two major parts. The first represents relatively higher molecular weight portion, and the second represents lower molecular weight portion. For sample A, not only the height of the first peak is lower, but also a trace peak at retention time of 10 h can still be discerned. As is known from the recipe in Table I, the mol ratio of resorcinol to lactose is 2. Suppose all lactose is subjected to completely hydrolysis during reaction, the mol ratio of R/L could still be around 1.5. More resorcinol may lower its condensing opportunities with lactose to form relatively larger molecules, as a result, it may cause the existence in free resorcinol, and lower molecular weight portion in the system. However, for samples B and C, the original mol ratios of R to L are 0.93 and 0.46, respectively; also, in lactose's hydrolysis during synthesis, there are enough aldehyde groups to condense with resorcinol. Thus, the chance of formation of relatively large molecules between lactose and resorcinol could be effectively increased with the decrease in resorcinol content, because, based on the reaction mechanism, one resorcinol molecule could simultaneously react with two lactose at the 4- and 6-carbon position. SEC's results for sample B and C in Figure 4 further confirm this assumption: there are no free resorcinol, and the larger molecular weight portion also increases with the decrease in resorcinol content.

The catalysis effect of phosphoric acid on the synthesis of R/L resin is evident. As can be seen in Figure 5, when mol ratio of lactose and resorcinol is fixed, the decrease in phosphoric acid can cause more unreacted resorcinol. Particularly, if phosphoric acid used is reached to 1.5 g as in the recipe of sample E, the original two peaks become one, with a longer retention time; than pure resorcinol peak appears. Also, another unknown peak shows at the retention time of 5.5 h. This indicates that the condensation reaction of one resorcinol with two lactose may be not strong enough to take place. Thus, it is clear that catalysis of phosphoric acid is very significant. It may offer protons to activate the aldehyde groups in lactose, and may cause lactose to be hydrolyzed into glucose, and make them more reactive with resorcinol. With the increase in phosphoric acid, the unreacted resorcinol

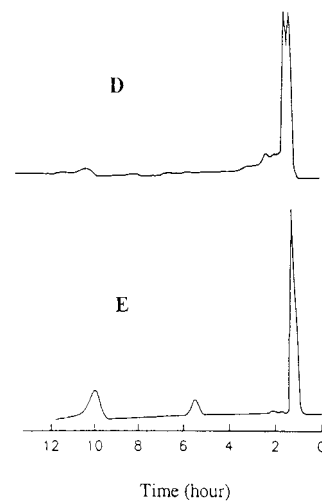


Figure 5 SEC spectra of resorcinol/lactose resins synthesized with different content of phosphoric acid.

in R/L resins reduces, and the larger molecular weight portion increases accordingly (as can be seen from sample B and C in Fig. 4). The result clearly indicates that the content of phosphoric acid can play a very important role in the condensation reaction between lactose and resorcinol.

Applications

Lactose-based resorcinol resin already shows some potential applications in many industrious fields. First, based on our primary result, it can directly react with 10% of hexamethyleneteramine at 100°C to produce a reddish chemically crosslinked solid with higher modulus and good boiling water resistance. The material can be used as an excellent adhesive for plywood and other related industries. The resin can also be used as a curing agent for epoxy, phenol, and amino resins. Furthermore, it can be blended with certain polymers, such as poly(methyl methacrylate) and poly(vinyl acetate) to modify their physical properties via chemical reaction or intermolecular interaction. More research in these fields are currently being undertaken in our lab.

CONCLUSIONS

A lactose-based resorcinol resin can be synthesized by reacting lactose with resorcinol under 95°C using phosphoric acid as the catalyst. ¹³C-NMR measurement indicates that the condensation reaction happened at the 4- or 6-carbon position in the benzene ring. SEC results show that the resin consists of two major parts with different molecular weights. The data also show that phosphoric acid is an effective catalyst for the resin synthesis.

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