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Condensation reactions of phenolic resins. 1. Kinetics and mechanisms of the base-catalyzed self-condensation of 2-hydroxymethylphenol[☆]

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Abstract

There are many discrepancies in the interpretations of the condensation of hydroxymethylphenols. Further investigation, reexamination of the kinetics in particular, is needed to clarify the reaction mechanisms. In this paper, the kinetic aspects of the base-catalyzed self-condensation of 2 hydroxymethylphenol (2-HMP) are discussed. The order of reaction was determined from the dependence of the initial rate of reaction on the initial concentration of 2-HMP. It was confirmed that the reaction is kinetically of genuine first-order. Consequently, any S_N2 mechanisms must be ruled out. A quinone methide intermediate hypothesis seems to hold: the dependence of reaction rate on the NaOH/2-HMP molar ratio could be explained kinetically based on the hypothesis. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Phenolic resin; 2-Hydroxymethylphenol; Self-condensation

1. Introduction

Alkaline phenol–formaldehyde resin is one of the most important adhesives for manufacturing composite wood materials for structural use. Its usefulness will be greatly widened if the curing conditions (high temperature and long time) needed for this resin is mitigated. Some chemicals (sodium carbonate, propylene carbonate, etc.) are known to have cure-accelerating effects. To elucidate the cure-accelerating actions of those chemicals and to seek further improvement, the kinetics and mechanisms of the curing reactions need to be clarified. The major part of the cure is attributed to the condensation reactions of hydroxymethylphenols (HMPs). Many papers have been published on the kinetics and mechanisms of the condensation reactions of HMP monomers as model compounds. However, there are many discrepant experimental results and interpretations [1]. Sprung and Gladstone studied the condensation of 2-hydroxymethylphenol (2-HMP) in a non-solvent system [2]. They say that the self-condensation of 2-HMP without any catalyst is kinetically of second-order, while it is of first-order in the presence of a base catalyst (triethanolamine). Yeddanapalli and Francis observed the base-catalyzed self-condensations of 2-HMP and 4-hydroxymethylphenol in an aqueous system to be kinetically of first-order [3]. They say, however, that the reaction is of pseudo first-order. They consider that the reaction is between the phenolate ion (dissociated HMP) and undissociated HMP molecule, but since the former is constant for a constant alkali concentration, the reaction appears to be of first-order. And they suggested a S_N2 mechanism in which a methylene carbonium ion (formed through a transition state involving hydrogen bonding between the methylol oxygen and aromatic hydrogen of another phenol) reacts with the negatively charged *ortho* or *para* position of a phenolate ion. Later, they revised the above idea and suggested that the small positive charge formed on the methylol carbon due to the electron attracting nature of the hydroxyl oxygen attacks centers of high electron density [4]. The S_N2 mechanism, in which the negatively charged 2- or 4-position of the quinoid structure attacks the methylol carbon of another molecule, has been introduced in many textbooks. In contrast with these ideas, Jones proposed a quinone methide intermediate hypothesis [5]. He says that the self-condensation of 2,4,6-trihydroxymethylphenol (THMP) is a first-order reaction. And, he derived a rate equation that involves the formation of quinone methide as the rate-determining step. Incidentally, as to the self-condensation of THMP, Freeman reported it as of first-order [6], while Sekhar and others reported it as of second-order [7] and Tohmura and others explained the

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dependence of the reaction rate on the alkali/THMP molar ratio assuming a S_N2 mechanism [8]. As to the kinetics of the self-condensation of dihydroxymethylphenols (DHMPs), Francis and Yeddanapalli obtained apparent first-order rate-constants for the disappearance of 2,4- and 2,6-DHMPs [4]. However, as mentioned above, they consider the reactions as of pseudo first-order. Which of the mechanisms is true? Or, do the mechanisms vary with the species of reactant? In addition, we notice that there are differences in the reaction conditions among the studies reported. Do the mechanisms change with the reaction conditions, too? We cannot obtain the answers from the studies reported until now. We notice that almost all of the previous kinetic studies adopted only a graphing method that plots a function of the reactant concentration against the reaction time, e.g. $\log(a - x)$ vs. t or $x/(a - x)$ vs. t. This graphing method, however, sometimes leads to misunderstanding. It gives correct results only in the case where reaction products have no effect on the reaction. In the base-catalyzed condensation of HMPs, reaction products take part in the reactions with the starting reactant. That is, the rate of reaction in terms of the decrease in the concentration of the starting reactant, $-\mathrm{d}[\mathrm{A}]/\mathrm{d}t$, cannot be expressed in a simple form composed of only one term regarding the function of the concentration of A. It makes a complicated form as shown below:

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_1 f[\mathrm{A}] + k_2 f[\mathrm{A}] f[\mathrm{B}] + k_3[\mathrm{A}] f[\mathrm{C}] + \cdots \quad (1)$$

where B and C represent the reaction products. Moreover, there can be two starting reactants, dissociated HMP and undissociated HMP, and the concentrations of the two reactants cannot be expressed by the functions of total amount of HMP except in the initial stage of reaction, because the reaction products, too, can dissociate affecting the dissociation equilibrium. Thus, each of the condensation reactions of HMPs needs to be reexamined. The most reliable way of determining the order of reaction is to observe the dependence of the initial reaction rate on the initial concentration of reactant. In this paper we report the results of the reexamination on the self-condensations of 2-HMP and discuss the reaction mechanisms.

2. Experimental

2.1. Materials

2-HMP (99%) was purchased from Aldrich Chemical Company Inc.

2.2. Analysis of the self-condensation reaction of 2-HMP

2-HMP was dissolved in an aqueous sodium hydroxide (NaOH) solution at room temperature, and then 1-ml portions of the solution were sealed in glass ampules. Each ampule was immersed in a constant-temperature bath for its allotted time to make the reaction progress. Then the ampule was cooled in an ice-containing bath and thereafter it was diluted with acetonitrile–water solution containing acetic acid of a required amount for neutralizing the reaction system. After being made a known volume with the use of a volumetric flask, the reaction system was subjected to high performance liquid chromatography (HPLC) and liquid chromatography-mass spectrometry (LC/MS) analyses. The self-condensation reactions were carried out with various initial concentrations of 2-HMP and NaOH/2-HMP molar ratios. A carbonate-free aqueous NaOH solution and degassed deionized-water were used. For the identification of reaction products, fractions collected by a preparative HPLC system were subjected to nuclear magnetic resonance (NMR) analyses. The changes in the concentration of 2-HMP during the reaction were calculated from the corresponding peak areas of the HPLC chromatograms. The rate of reaction at an arbitrary time was determined as $([\text{2-HMP}]_{t1} - [\text{2-HMP}]_{t2})/(t_2 - t_1)$, and it was plotted against time, $(t_2 - t_1)/2$, and the value at time zero obtained by extrapolation was taken as the initial rate of reaction (R_i), where $[\text{2-HMP}]_{t1}$ and $[\text{2-HMP}]_{t2}$ denote the concentrations of 2-HMP at time t_1 and t_2, respectively. The dependence of R_i on the initial concentration of 2-HMP ($[\text{2-HMP}]_i$) was investigated with fixed NaOH/2-HMP molar ratios.

2.3. HPLC analysis

A Shimadzu 10AD liquid chromatograph was used. The following conditions were adopted: column: Intersil ODS-3 (5 μm, 4.6 × 250 mm) (GL SCIENCE); solvent: water–acetonitrile gradient system (starting with the water–acetonitrile volume ratio of 5/95, 50/50 at 10 min, 0/100 after 25 min); flow rate: 1.0 ml/min; column temperature: 25°C; detection: UV 280 nm.

2.4. LC/MS analysis

A HITACHI M-1200 AP/ES Mass spectrometer was used. The following conditions were used: column, solvents, gradient ratios, column temperature, flow rate and detection in the LC part: the same as those in the HPLC analysis; ionization: APCI (negative); neubulizer temperature: 300°C; desolvator temperature: 400°C; drift: 60 V.

2.5. NMR analysis

A JEOL JNM-AL 400 FT NMR Spectrometer was used. ^{1}H and ^{13}C NMR spectra were obtained with the use of deuterated dimethyl sulfoxide (DMSO-d_6) as a solvent and tetramethylsilane as the internal standard.

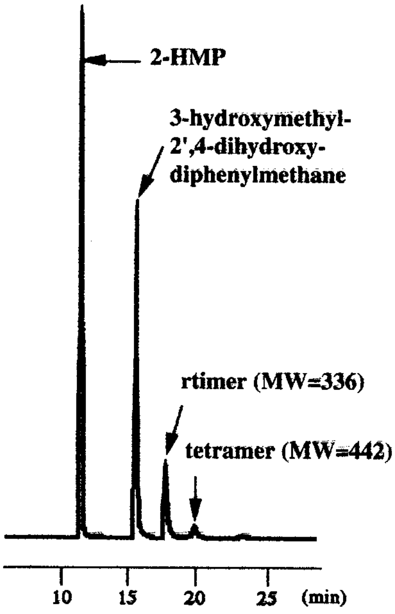

Fig. 1. HPLC chromatogram of a reaction system. Reaction conditions: $[\text{2-HMP}]_i$, 0.2 mol/l; NaOH/2-HMP molar ratio, 0.1; temperature, 100°C; time, 180 min.

3. Results and discussion

3.1. Reaction products in the early stage of reaction

Fig. 1 shows a HPLC chromatogram of the reaction system. Four absorption peaks in this chromatogram were assigned to 2-HMP, a dimer with molecular weight (M_W) of 230, a trimer with MW of 336 and a tetramer with M_W of 442 by LC/MS analysis. ^{13}C NMR analysis identified the dimer as 3-hydroxymethyl-2′, 4-dihydroxy-diphenylmethane showing the signals of *ortho–para* methylene carbon at 34.5 ppm and *ortho*-methylol carbon at 58.4 ppm. There could be detected no *ortho–ortho* methylene-bonded dimer in the early stage of reaction. Fig. 2 shows an example of reaction time-course. In this figure, the amounts of 2-HMP and reaction products are shown in terms of the peak areas in the HPLC chromatograms, not in terms of moles per liter because of the lack of data on the molar UV-absorption intensities of the reaction products. The pattern of the formation of reaction products did not vary with the initial concentration of 2-HMP, with the NaOH/2-HMP molar ratio and with reaction temperature.

3.2. Order of reaction

Fig. 3 shows examples of $\log(a - x)$ vs. t plot for reference. Here, a and x denote the initial concentration of 2-HMP and the decrease in the concentration of 2-HMP at reaction time t, respectively. Linear relationships can be observed between $\log(a - x)$ and t. However, this is merely an appearance, and it does not necessarily mean that the order of reaction is unity. As seen in Fig. 2, the formation of a trimer starts in an early stage of reaction and becomes significant as the reaction progresses. That is, the decrease in the amount of 2-HMP includes not only that due to the reaction of 2-HMP with 2-HMP but also that due to the reaction of a dimer with 2-HMP. To determine the order of reaction strictly, the dependence of the rate of reaction on the initial concentration in the very early stage must be investigated. Fig. 4 shows the R_i vs. $[\text{2-HMP}]_i$ plot. As this figure shows, R_i is proportional to $[\text{2-HMP}]_i$. This relationship did not change with the NaOH/2-HMP molar ratio and reaction temperature. Thus, it can be said that the order of reaction is 1.0. That is, the following equation holds:

$$R_i = (-\mathrm{d}[\text{2-HMP}]/\mathrm{d}t)_i = k[\text{2-HMP}]_i \tag{2}$$

3.3. Dependence of R_i on the NaOH/2-HMP molar ratio

The rate of reaction increases with an increase in the

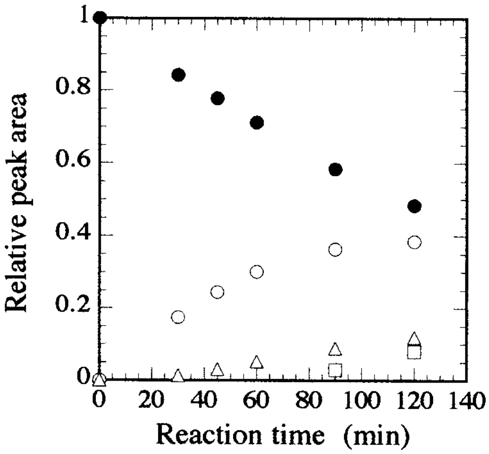

Fig. 2. A time-course of the formation of reaction products. ●, 2-HMP, ○, dimer, △, trimer, □, tetramer. Reaction conditions: $[\text{2-HMP}]_i$, 0.2 mol/l; NaOH/2-HMP molar ratio, 0.1; temperature, 100°C.

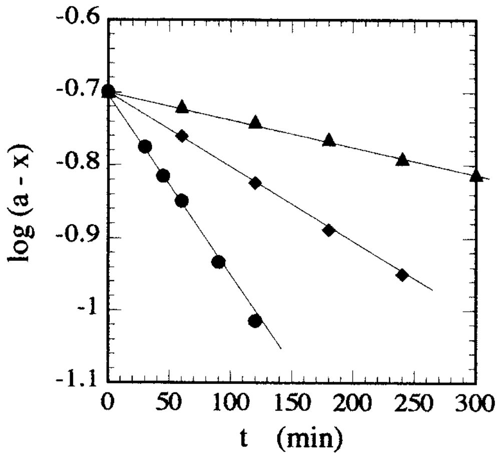

Fig. 3. Examples of $\log(a - x)$ vs. t plot. Reaction conditions: $[\text{2-HMP}]_i$, 0.2 mol/l; NaOH/2-HMP molar ratio, 0.1; ▲,, 80°C; ◆, 90°C; ●, 100°C.

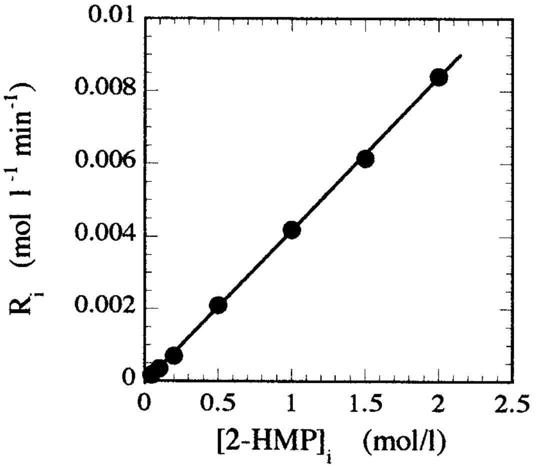

Fig. 4. Initial rates of reaction plotted against the initial concentrations of 2-HMP. Reaction conditions: temperature, 100°C; NaOH/2-HMP molar ratio, 0.5.

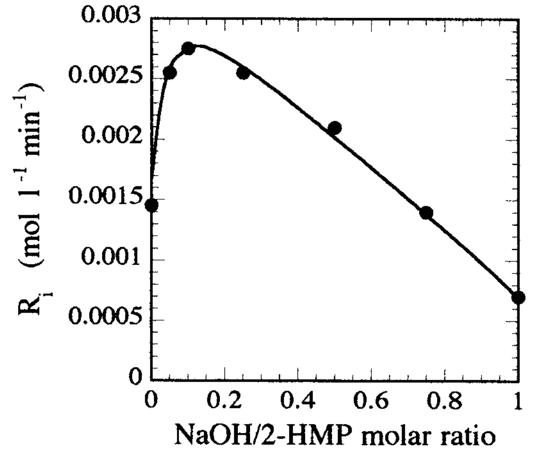

Fig. 6. Comparison of the values of R_i calculated by Eq. (9) with those observed experimentally. ●, observed, —, calculated. Reaction conditions: temperature, 100°C; [2-HMP]$_i$, 0.5 mol/l.

NaOH/2-HMP molar ratio until it reaches the maximum at around the NaOH/2-HMP molar ratio of 0.1, thereafter it decreases as the molar ratio increases (Fig. 6).

3.4. Energy of activation

The energy of activation was found to be 103 ± 5 kJ/mol from the Arrhenius plots of the values for R_i obtained at 80, 90 and 100°C with [2-HMP]$_i$ of 0.2 mol/l and NaOH/2-HMP molar ratios of 0.05, 0.1, 0.5 and 0.75. This value is greater than those reported by Sprung and Gladstone (18.5 kcal/mol) and Yeddanapalli and Francis (16.0 kcal/mol).

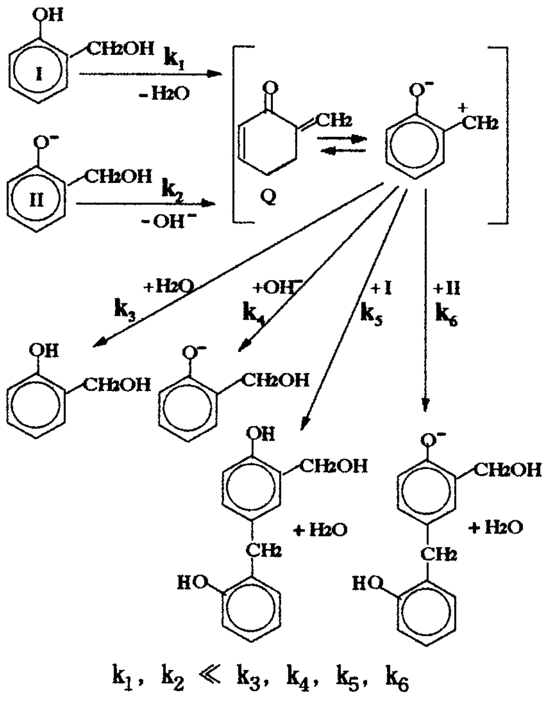

Fig. 5. Quinone methide intermediate hypothesis applied to the self-condensation of 2-HMP.

3.5. Mechanisms of reaction

As confirmed above, the reaction is genuinely of first-order, not of pseudo first-order. Therefore, any S_N2 mechanisms must be ruled out. Thus, we must find out a mechanism in which the formation of activated complex by unimolecular reaction makes the rate-determining step. A quinone methide intermediate hypothesis has been proposed by Jones to explain the kinetics of the self-condensation of THMP [5]. We examined the application of this hypothesis to the case of 2-HMP. It is considered that quinone methide exists in the form of a resonance hybrid between quinoid and benzenoid structure [1]. Thus, the self-condensation of 2-HMP can be illustrated as shown in Fig. 5. And the following rate equations can be obtained:

$$\begin{aligned} \mathrm{d}[\mathrm{Q}]/\mathrm{d}t = {} & k_1[\text{2-HMPH}] + k_2[\text{2-HMP}^-] - [\mathrm{Q}](k_3[\mathrm{H_2O}] \\ & + k_4[\mathrm{OH}^-] + k_5[\text{2-HMPH}] + k_6[\text{2-HMP}^-]) = 0 \end{aligned} \tag{3}$$

$$\begin{aligned} [\mathrm{Q}] = {} & (k_1[\text{2-HMPH}] + k_2[\text{2-HMP}^-])/(k_3[\mathrm{H_2O}] + k_4[\mathrm{OH}^-] \\ & + k_5[\text{2-HMPH}] + k_6[\text{2-HMP}^-]) \end{aligned} \tag{4}$$

$$\begin{aligned} -\mathrm{d}[\text{2-HMP}]/\mathrm{d}t & = (k_5[\text{2-HMPH}] + k_6[\text{2-HMP}^-])[\mathrm{Q}] \\ & = (k_5[\text{2-HMPH}] + k_6[\text{2-HMP}^-])(k_1[\text{2-HMPH}] \\ & \quad + k_2[\text{2-HMP}^-])/(k_3[\mathrm{H_2O}] + k_4[\mathrm{OH}^-] \\ & \quad + k_5[\text{2-HMPH}] + k_6[\text{2-HMP}^-]) \end{aligned} \tag{5}$$

where Q represents quinone methide, and 2-HMPH and 2-HMP$^-$ denote undissociated 2-HMP and dissociated

2-HMP, respectively. Here, the following relationships hold:

$$[\text{2-HMPH}] + [\text{2-HMP}^-] = [\text{2-HMP}] \quad (6)$$

$$[\text{2-HMPH}] = [\text{2-HMP}]/(1 + K_a[\text{OH}^-]/K_w) \quad (7)$$

$$[\text{2-HMP}^-] = [\text{2-HMP}](K_a[\text{OH}^-]/K_w)/(1 + K_a[\text{OH}^-]/K_w) \quad (8)$$

where K_a and K_w represent the dissociation constant of 2-HMP and the ion product of water, respectively. Thus, Eq. (5) converts into the following equation:

$$-\mathrm{d}[\text{2-HMP}]/dt = [\text{2-HMP}]^2\{k_5/(1 + \mathrm{A}) + k_6\mathrm{A}/(1 + \mathrm{A})\} \times\{k_1/(1 + \mathrm{A}) + k_2\mathrm{A}/(1 + \mathrm{A})\}/\{(k_3[\mathrm{H_2O}] + k_4[\mathrm{OH}^-] + [\text{2-HMP}](k_5/(1 + \mathrm{A}) + k_6\mathrm{A}/(1 + \mathrm{A}))\} \quad (9)$$

where A is $K_a[\mathrm{OH}^-]/K_w$.

Although the rate equation was obtained as above, we have no means to determine the values of rate constants individually. Therefore, we made numerical calculations to find out a set of rate constant values that fit the experimental data. That is, we put a set of values on the six rate constants in Eq. (9) and calculated the values of R_i at various NaOH/2-HMP molar ratios, and then compared them with the experimental ones. Modification of the values of rate constants was continued until the calculated values of R_i agreed with the experimental ones. It was assumed that the temperature dependence of K_a was the same as that of K_w. Values 84.39×10^{-10} and 58.2×10^{-14} were adopted as K_a and K_w at 100°C, respectively, and $[\mathrm{OH}^-]$ was calculated numerically by the method described in our previous paper [9]. Fig. 6 shows the result. As seen in this figure, we can obtain a set of values for the rate constants so that the dependence of the reaction rate on the NaOH/2-HMP molar ratio can be explained by Eq. (9). The values of rate constants found are as follows:

$$k_1 = 6.8 \times 10^{-3}\ \mathrm{min}^{-1} \quad k_2 = 1.5 \times 10^{-3}\ \mathrm{min}^{-1}$$

$$k_3 = 2.5 \times 10^5\,\mathrm{l\ mol}^{-1}\ \mathrm{min}^{-1}$$

$$k_4 = 2.0 \times 10^8\,\mathrm{l\ mol}^{-1}\ \mathrm{min}^{-1}$$

$$k_5 = 2.5 \times 10^5\,\mathrm{l\ mol}^{-1}\ \mathrm{min}^{-1}$$

$$k_6 = 2.0 \times 10^7\,\mathrm{l\ mol}^{-1}\ \mathrm{min}^{-1}.$$

Thus, the quinone methide intermediate hypothesis seems to hold. However, it must be noted that we have no other means to verify the values of rate constants obtained. Incidentally, Lenghaus and others say that an *ortho* quinone methide intermediate is very site specific, preferring to react at a free *ortho* site of phenols [10]. This conflicts the quinone methide intermediate hypothesis for the self-condensation of 2-HMP where the formation of *ortho*–*para* methylene bond is predominant. However, it must be noted that the reaction conditions are very different: they used 2-hydroxymethyl-4,6-dimethylphenol as a model compound and carried out the reactions of it with itself and other phenols in a melt state without alkali.

4. Conclusion

Observation of the dependence of the initial reaction rate on the initial reactant concentration revealed that the self-condensation of 2-HMP is of genuine first-order. Consequently, any $\mathrm{S_N2}$ mechanisms must be ruled out. The dependence of the reaction rate on the NaOH/2-HMP molar ratio could be explained kinetically by a rate equation based on a quinone methide intermediate hypothesis. Thus, the hypothesis seems to hold in the case of 2-HMP.

References

[1] Knop A, Pilato LA. Phenolic resins. Berlin: Springer, 1985 (p. 40–6).

[2] Sprung MM, Gladstone MT. J Am Chem Soc 1949;71:2907–13.

[3] Yeddanapalli LM, Francis DJ. Macromol Chem 1962;55:74–86.

[4] Francis DJ, Yeddanapalli LM. Macromol Chem 1969;125:119–25.

[5] Jones R. J Polym Sci, Polym Chem Ed 1983;21:1801–17.

[6] Freeman JH. Am Chem Soc Div Org Coat Plat Chem Pap 1967;27(1):84–99.

[7] Sekhar N, Kuchrska H, Vasishth RC. Am Chem Soc Div Polym Chem Polym Prepr 1971;12(1):585–92.

[8] Tohmura S, Hattori Y, Higuchi M, Sakata I. Mokuzai Gakkaishi 1994;40(4):390–8.

[9] Higuchi M, Nohno S, Tohmura S. J Wood Sci 1998;44:198–203.

[10] Lenghaus K, Qiao GG, Solomon DH. Polymer 2000;41:1973–9.