



# Gelation and cross-link inhomogeneity of phenolic resins studied by small- and wide-angle X-ray scattering and $^1\text{H}$ -pulse NMR spectroscopy



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## ABSTRACT

The gelation mechanism and cross-link inhomogeneity of phenolic resins prepared via polycondensation of phenol and formaldehyde under acidic conditions were studied using small- and wide-angle X-ray scattering and  $^1\text{H}$ -pulse nuclear magnetic resonance spectroscopy. The solvent-swelling technique was applied for both measurements at the initial stage of gelation to enhance the local fluctuations of the cross-link density. The change in the static and dynamic structures obtained through observations of the X-ray scattering functions and the spin–spin relaxation functions, respectively, during the polycondensation reaction indicates the presence of two different mechanisms for the formation and growth of the inhomogeneity that depend on the amount of cross-linker. (i) When there is a stoichiometrically insufficient amount of the cross-linker, inhomogeneous domains with a loosely cross-linked network appear at the initial stage of gelation. The intradomain reactions become dominant in the growth of the inhomogeneous domain and the degree of cross-linking in the domain increases by bridging two unreacted sites in the network structure via the cross-linker. (ii) When there is a stoichiometric amount of the cross-linker, inhomogeneous domains with a tightly cross-linked network appear at the initial stage of gelation. The interdomain reactions become dominant in the growth of the domain and the size of the domain increases by incorporating new polymer chains into the domain via the cross-linker.

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## 1. Introduction

Phenolic resins were the first artificial plastics developed that were based on a synthetic polymer, and were invented by Baekeland in 1907. Because of their excellent mechanical properties as well as heat and solvent resistance, they have been employed as insoluble and infusible thermosetting resins in electronics, automotive, housing, and other industries [1]. The basic chemical structure of phenolic resins comprises a three-dimensional cross-linked network of three functional phenols and two functional methylenes. Three methylenes can connect to a phenol, one at the *para*-position and the other two at the two *ortho*-positions that are adjacent to the hydroxyl group of the phenolic ring. This cross-

linked network provides the abovementioned desirable properties and it is believed that the inhomogeneity of the cross-linked structure influences these properties. However, structural analysis of phenolic resins is difficult because of their insolubility in common organic solvents and their infusibility. Therefore, elucidation of their cross-linked structure and inhomogeneity has been one of the major challenging objectives of the structural analysis of phenolic and other thermosetting resins. The definition of “inhomogeneity of thermosetting resins” is well summarized in the literature [2,3].

It is well known that the case of the inhomogeneity of phenolic resins was first raised by de Boer and Houwink in 1936 [4,5]. As described in our previous paper [6], arguments regarding the inhomogeneity of phenolic and other thermosetting resins, and their structure–property relationships persist even today through observations using scanning and transmission electron microscopy [7–13], atomic force microscopy [12,14,15], small- and wide-angle X-ray scattering (SAXS and WAXS, respectively), and small-angle neutron scattering (SANS) [2,6,16–21].

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Of these methods, SANS and SAXS have proven to be powerful techniques for elucidating the cross-link inhomogeneity of gel networks [22–28]. In most cases, these scattering methods utilize the swelling feature of the gel; swelling enhances the local fluctuations of the cross-link density because the degree of swelling depends on the degree of cross-linking. The enhancement of the spatial inhomogeneity of the gel network results in a large scattering contrast. However, it is difficult to apply this solvent-swelling technique to highly cross-linked thermosetting resins and only a few studies have addressed cross-link inhomogeneity in phenolic and other thermosetting resins using these scattering methods as compared to the number of SEM and TEM studies of inhomogeneity.  $^1\text{H}$ -pulse nuclear magnetic resonance (NMR) spectroscopy is also one of the most promising techniques for elucidating the cross-link inhomogeneity of gel networks [29–35].  $^1\text{H}$ -pulse NMR spectroscopy offers the spin–spin relaxation time of protons, which is related to the mobility of molecules to which the protons are attached; the lower the molecular mobility, the shorter the relaxation time. For cross-linked polymers, the molecular mobility of polymer segments strongly depends on their local cross-link density [36] and the spin–spin relaxation of tightly cross-linked segments with lower molecular mobility decays faster than that of loosely cross-linked segments.

For theoretical understanding of the cross-linked network structure and the structure–property relationships of phenolic and other thermosetting resins, computer simulations, such as statistical and kinetic methods, molecular dynamics (MD) simulations, and Monte Carlo (MC) simulations, are also promising tools because they are not limited by polymer solubility and infusibility, which always cause experimental difficulties in structural analyses [37–44]. Yamagishi et al. investigated the gelation mechanism of phenolic resins using MC simulations with the cubic percolation theory [41]. According to the simulation results for a polycondensation system with an initial formaldehyde-to-phenol molar ratio of 1.2, the intramolecular reaction occurred more frequently in the gel cluster with increasing gel fraction beyond the gel point and resulted in network formation inside the gel. Unfortunately, this significant result for the gelation mechanism of phenolic resins has not yet been precisely evaluated experimentally except for our previous SAXS study [6].

We have been focusing on understanding the inhomogeneity and structure–property relationships of phenolic resins using scattering methods and MD simulations [6,20,21,44,45]. Through these investigations, we concluded that the characterization of the formation and growth mechanisms of gel networks could be important for elucidating the inhomogeneity of fully cured phenolic and other thermosetting resins, because the cross-link

inhomogeneity has not been observed for the cured phenolic resins prepared with different amounts of the cross-linking agent by either SANS, SAXS, or SEM studies. In our previous study [6], the gelation mechanisms of phenolic resins have been investigated through solid-state  $^{13}\text{C}$  NMR, SAXS, and reaction kinetics including the successful application of this solvent-swelling technique in SAXS analysis at the initial stage of gelation. This provided new gelation mechanisms for the formation and growth of the cross-link inhomogeneity that depend on the amount of cross-linker: (i) when there is a stoichiometrically insufficient amount of the cross-linker, inhomogeneous domains with a loosely cross-linked network appear at the initial stage of gelation and the degree of cross-linking in the domain increases with the reaction time. On the other hand, (ii) when there is a stoichiometric amount of the cross-linker, inhomogeneous domains with a tightly cross-linked network appear at the initial stage of gelation, followed by an increase in the size of the domain. This result of our previous study agrees well with Yamagishi's simulation result; however, additional experimental verification is required to confirm and refine the gelation mechanism.

In this study, we have further investigated the gelation mechanisms of phenolic resins using SAXS, WAXS, and  $^1\text{H}$ -pulse NMR spectroscopy. The solvent-swelling technique was applied at the initial stage of gelation for all measurements to enhance the local fluctuations of the cross-link density.

## 2. Experimental

### 2.1. Materials

Phenol, 37 wt% formaldehyde aqueous solution, anhydrous oxalic acid, tetrahydrofuran (THF), and THF- $d_8$  with a 99.5% degree of deuteration were purchased from Wako Pure Chemical Industries, Ltd. (Japan). All materials were used without further purification.

Novolac-type phenolic resins **NV12** and **NV15** were prepared via the polycondensation of phenol and formaldehyde with oxalic acid as an acid catalyst, as shown in Fig. 1. The initial molar ratios of phenol/formaldehyde/oxalic acid were 1.0/1.2/0.010 for **NV12** and 1.0/1.5/0.010 for **NV15**. Note that the reaction was performed in a tightly-sealed vial to avoid any slight change in the molar ratio caused by volatilization of the monomers. The initial formaldehyde-to-phenol molar ratios of **NV12** and **NV15** corresponded to off-stoichiometric and on-stoichiometric ratios, respectively, which resulted in polycondensation reactions with a stoichiometrically insufficient amount of the cross-linker and a stoichiometric amount of the cross-linker, respectively. The

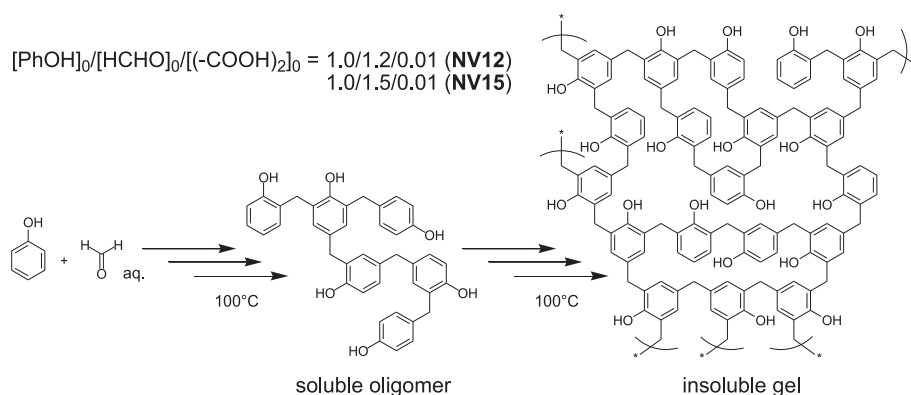


Fig. 1. Polycondensation of phenol and formaldehyde.

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