# Structure and curing mechanism of high-ortho and random novolac resins as studied by NMR

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### ARTICLE INFO

### ABSTRACT

^{1}H pulse NMR and ^{13}C CPMAS NMR measurements are carried out for novolac resins in order to investigate the structure and curing mechanism. Thermal behavior of molecular mobility obtained from spin–spin relaxation time, $T_2$, indicates that the hydrogen bond network formed in novolacs is predominant factor of glass transition for novolacs without cross-link agents. In presence of cross-link agent, hexamethylenetetramine (HMTA), the appearance of adducts between novolacs and HMTA is recognized. At curing temperature, the rigid fraction increased as a final step of curing. Different thermal behavior of mobility is observed for random and high-ortho novolacs/HMTA. Formation of adducts occurred at lower temperature for high-ortho novolac. ^{13}C NMR chemical shift and quantum chemical calculation suggest that high acidity of phenolic OH of o-novolac caused by intramolecular hydrogen bonding is responsible for the formation of adducts at lower temperature.

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## 1. Introduction

Novolac resin which is acid-catalyzed phenol–formaldehyde thermosetting resin, is used for various industrial materials such as binding material, shell molding agent, curing agent of epoxy resin, brake friction materials and so on [1]. Formaldehyde and phenol are reacted to promote electrophilic addition of formaldehyde to the ortho and para substitutions of phenol ring. Two kinds of novolacs, high-ortho and random novolacs in which the ortho/para ratios are different are used commercially. The random novolac is used as a standard novolac which is cured with hexamethylenetetramine (HMTA). The obtained fully cured phenolic resin is used for various applications. For the application which needs quick curing, the high-ortho novolac is used for acceleration of curing in the presence of HMTA, because the phenol ring carbon of the para site has an advantage in reaction with HMTA, giving rise to formation of cross-links at a high rate.

A great deal effort has been expended for clarifying the curing chemistry of phenolic resin. However, because the curing reactions are complicated and the resultant phenolic resin is cross-linked, most available analytical techniques are difficult to investigate the curing reaction mechanism for phenolic resin.

As the first step for clarifying the curing mechanism, Fyfe et al. [2] applied high-resolution ^{13}C NMR spectroscopy using cross polarization magic angle spinning (CPMAS) technique to the direct investigation of solid cured phenolic resins. Bryson et al. [3] reported ^{13}C NMR study of solid phenolic resins using CPMAS, where they made ^{13}C peak assignments of high-ortho and random novolac resins and discussed of curing process. Zhang et al. [4,5] studied chemistry of novolac resins on curing with HMTA by means of ^{13}C and ^{15}N NMR spectroscopy with special reference to the chemical shift assignments and reactivity of the ortho/para sites of the curing intermediates.

On the other hand, estimation of degree of curing is important practically because the degree of curing is closely associated with physical properties of phenolic resin. For instance, if the degree of curing is insufficient, thermal stability decreases. For this purpose, however, the above-mentioned high-resolution NMR methods have a disadvantage that it takes long time to acquire spectra with sufficient signal-to-noise ratio. Usually, novolacs are cured at high temperature for several minutes. If ^{13}C CPMAS NMR used to estimate the degree of curing, more than one hour is needed to observe a spectrum which can afford the detailed chemical shifts. *In-situ* detection of the curing state requires the enhancement of sensitivity such as the isotopical labeling.

^{1}H pulse NMR spectroscopy of solid polymers gives spectra with high sensitivity and measuring time as short as orders of second if the sample is sufficient enough [6,7]. From ^{1}H pulse NMR, relaxation times such as spin–lattice relaxation time ($T_1$), spin–spin

relaxation time ($T_2$) can be obtained. It is obvious that the frequency dependence of $T_1$ and $T_2$ offers precise information about the state of molecular motion [8]. From the practical point of view, since the frequency dependence of relaxation times requires machines which can change magnetic field, the application seems to be limited.

Adriaensens et al. [9] studied the cure state of high-ortho novolac resin by means of $^1$H wide-line and $^{13}$C CPMAS spin–lattice ($T_{1H}$) relaxation solid-state NMR as a function of temperature. It was revealed that mobile end groups and branches determine the most efficient pathway of $T_{1H}$ relaxation. Due to the spin diffusion by strong dipolar coupling in the solid state, $T_1$ is averaged out over for several tens of nm.

Litvinov used $^1$H NMR to investigate the phase composition, molecular mobility, network structure of vulcanized EPDM/PP thermoplastic [10]. The network density, cross-link, the density of chemical or physical cross-link were estimated through $T_2$.

Neiss and Vanderheiden [11] reported solution and solid-state NMR analysis of phenolic resin cure kinetics and obtained a result that $^1$H wide-line solid-state NMR can be used to measure the rate of sample curing *in situ* by monitoring $T_2$ relaxation time of the whole sample as a function of sample heating time. As $T_2$ is not affected by spin diffusion in the solid state and can be measured in a short time enough used for *in situ* measurements, $T_2$ seems to be appropriate for estimation of curing state.

In order to clarify the curing mechanism for phenolic resin with special reference to the reactivity and mobility of novolac resin in the course of curing process, it is worthy to investigate a relationship between the detailed cross-linked structure and the molecular mobility on curing. In this paper, we will report on the curing mechanism of high-ortho and random novolac resins by means of $^1$H and $^{13}$C NMR in the solid state.

## 2. Experimental

### 2.1. Sample

High-ortho (o-novolac) and random novolac (r-novolac) resins were used as reactants for curing reaction. o-Novolac resin was prepared by reacting 500 g of phenol with 260 g of 37% formaldehyde solution in the presence of zinc diacetate (1.46 g) as a catalyst for 4 h under reflux. The reaction mixture was heated gradually to 160 °C by evaporating water and then unreacted phenol was removed by distilling under reduced pressure. r-Novolac resin was prepared in the presence of oxalic acid as a catalyst. The preparation procedure was same as o-novolac except the catalyst.

For curing experiments, mechanically powdered o- and r-novolacs and HMTA were mixed at a novolac/HMTA weight ratio of 93/7. The mixtures thus obtained were then cured at various temperatures at 60, 80,100, 120, 130, 140 and 150 °C and used for CPMAS measurements. Also, the mixtures are used for *in situ* $^1$H pulse NMR and TMA measurements.

### 2.2. Measurements

Solution $^{13}$C NMR spectra of the samples dissolved in methanol were recorded by a Bruker AVANCE DSX300 WB NMR spectrometer at resonance frequency of 75 MHz. o-Novolac and r-novolac were dissolved in methanol by adjusting the concentration about 5% and 5 mm NMR tube were used for measurements. Solution $^{13}$C NMR spectra were recorded by $^1$H decoupled single pulse sequence. The number of accumulations is 1024 and $\pi/2$ pulse was 10 μs. Methyl peak of methanol was set to be 49.05 ppm from TMS.

High resolution solid-state NMR measurements were carried out by using the same machine with solid accessory. High resolution solid-state spectra were measured for cured samples by using

CPMAS technique at ambient temperature. Samples were contained in a cylindrical 2.5 mm zirconia rotor and were spun at 10 kHz. CPMAS spectra were observed at a contact time of CP of 2 ms and a repetition time of 5s, a $\pi/2$ pulse width of 3 μs, spin lock field $B_1$ of 100 kHz and the number of accumulations is 1024. The magic angle was adjusted by using Br signal of KBr and Hartman-Hahn condition was adjusted by using adamantine. Up field peak of adamantine was set to be 29.47 ppm from TMS.

$^1$H pulse NMR measurements were performed by a JEOL MU25 NMR spectrometer at resonance frequency of 25 MHz. Measurements were carried out at every 10 °C by increasing the temperature from 30 to 160 °C. In order to correlate the reactivity and mobility of novolac resin in the course of curing process, it is necessary to measure $T_2$ in the range between the solid state and the state around melting. Since $T_2$ in the solid state is too short to be measured by Carr–Purcell–Meiboom–Gill (CPMG) because of the dead time effect after the pulse sequence, solid echo [12] pulse sequence ($90_x^\circ - \tau - 90_y^\circ$) was used for $T_2$ measurements. $\pi/2$ pulse width of 2 μs, $\tau$ of 8 μs and a repetition time of 5 s were used for solid echo measurements. The number of accumulations is 128. Free induction decay (FID) is obtained as a result of solid echo measurement.

Usually FID is composed of several components of $T_2$ decays with different mobility. It is known that the $T_2$ decay is expressed by simple exponential (Eq. (1)), Gaussian (Eq. (2)) and Weibullian/Sine functions [13]. Weibullian/Sine function is observed for the component in which the molecular motion is restricted such as crystalline phase. For amorphous polymers, $T_2$ decay is expressed as a sum of the following functions:

$$M(t) = A_1 \exp\left\{ -\frac{t}{T_{21}} \right\} \tag{1}$$

$$M(t) = A_2 \exp\left\{ -\left(\frac{t}{T_{22}}\right)^2 \right\} \tag{2}$$

where $T_{2i}$ is the spin–spin relaxation time of $i$th component and $A_i$ the fraction of the $i$th component. Analysis of the obtained FID carried out by computer fitting with Eqs. (1) and (2) and $T_{2i}$ and $A_i$ are obtained. In discussing $T_2$, the effect of magnetic field inhomogeneity becomes problem, i.e. $T_2 > T_2^*$. The effect of magnetic field inhomogeneity depends on the apparatus. If the contribution of the magnetic field inhomogeneity is effective, the shape of $T_2$ decay deviate from the above equations and $M(t)$ rapidly decreases [10]. This behavior is observed when FID data is collected for more than 1000 μs by solid echo method. Since data is acquired from 0 to 1000 μs, the obtained $T_2$ is unaffected by the magnetic field inhomogeneity in this study.

Thermal mechanical analysis was carried out by heating the samples from 60 to 170 °C at a rate of 5 °C/min in a MAC Science TMA 4000 under a sine-curve load with amplitude of 5 g and a period of 5 s.

## 3. Results and discussions

In Fig. 1a and b are shown solution $^{13}$C NMR spectra for o- and r-novolacs, respectively. $^{13}$C NMR chemical shifts and their assignments [4,11,14] are summarized in Table 1.

$^{13}$C chemical shift at 40.1, 35.1–33.9 and 31.1–29.8 ppm are attributed to the methylene carbons in para–para ($p$–$p'$), ortho–para ($o$–$p'$) and ortho–ortho ($o$–$o'$)-diphenylmethane type methylene bridges (RArCH$_2$ArR'), respectively. The percent content ($OR$) of CH$_2$ bonded to the ortho position of phenolic ring can be estimated from the following equation [14]:

$$OR(\%) = \frac{A(o-o') + \frac{A(o-p')}{2}}{A(o-o') + A(o-p') + A(p-p')} \times 100 \tag{3}$$