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ANALYSIS OF HYDROXYBENZENE-METHANAL OLIGOMERS USING ¹H NMR SPECTROSCOPY METHODS

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Abstract: The chemical structure of oligomers synthesized based on hydroxybenzene-methanal and 2,5-furandione at different ratios and temperature ranges was studied using quantitative NMR spectroscopy methods. In addition to methylene bridges and simple ether bonds between hydroxybenzene rings in hydroxybenzene-methanal resins, the formation of structural groups based on 2,5-furandione, as well as macromolecular transformations and the presence of fragmentary bonds, were observed. The mechanism of the polycondensation process of hydroxybenzene and methanal in an alkaline medium was investigated. Structural and functional differences in the composition of oligomers synthesized from hydroxybenzene-methanal and 2,5-furandione were identified.

Keywords: hydroxybenzene-methanal, 2,5-furandione, synthesis, oligomer, resin, spectroscopy, polycondensation, ether, methylene, proton.

Introduction. Phenol-formaldehyde resins are polycondensation products of phenolic compounds with formaldehyde and hold a significant position in the overall production of synthetic resins. As one of the first synthetic polymer materials, they remain valuable across numerous industries today. The development of production in many countries is driven by the continuously increasing demand from consumer sectors. On the other hand, phenol-formaldehyde resins are cost-effective, derived from abundant natural raw material sources, technologically simple to manufacture, and can be modified to control specific properties for a wide range of operational applications [1-5].

According to SRI Consulting, global production of phenol-formaldehyde resins reached approximately 5 million tons in 2014. The primary consumer sector—accounting for up to 35% of manufactured products—is the wood processing industry, including plywood, fiberboard, particleboard, oriented strand board, and other wood-based materials. Nearly equivalent demand exists in the foundry industry, thermal insulation materials, and laminated plastics production, which collectively account for 14%, 13%, and 12% of phenol-formaldehyde resin manufacturing, respectively [6-10]. Additionally, these resins are highly valuable for the production of paints, varnishes, abrasives, friction materials, adhesive compositions, foam plastics, coatings for various applications, sealants, and more.

The authors investigated and characterized the condensation mechanisms of formaldehyde with phenol in resole-type phenol-formaldehyde oligomers (PFOs) under well-controlled conditions, including temperature, stoichiometry, catalyst, and pH, using

high-performance liquid chromatography (HPLC) and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Their study described a two-step process for the formation of PFOs. In the first step, they examined the substitution of formaldehyde at the free ortho and para positions of the phenol ring. In the second step, they analyzed the self-condensation reaction between two molecules. Initially, under neutral or acidic conditions at 130°C, the formaldehyde molecule forms ether bonds and methylene bridges. In the final stage, the hydroxymethyl group undergoes an electrophilic attack on the aromatic ring proton [11].

Similarly, in another study, it was observed that ortho-substitution occurs in the early stages of PFO formation, along with the formation of a hemiacetal intermediate in the methylol derivative. These methylol-substituted intermediates are highly unstable, and the relative rate of structural formation can be better assessed by analyzing the methylene bridge region. According to ^{13}C NMR results, para-para bridges are formed first, followed by ortho-para and finally ortho-ortho linkages. The relative intensity analysis of ortho and para bridge carbon atoms provides insight into the isomeric composition of the final oligomer. The ratio of each isomer depends on the catalyst used in resin synthesis [12-13].

Hydroxybenzene-methanal oligomers were synthesized based on 2,5-furandione, and their kinetic and physicochemical analyses were conducted [14-18]. This research paper focuses on the structural characteristics of hydroxybenzene-methanal oligomers synthesized using 2,5-furandione. The structural investigation was performed using ^{1}H NMR spectroscopy to analyze the resin composition. The synthesis of hydroxybenzene-methanal oligomers was carried out at different molar ratios and temperatures, and the obtained products were examined. NMR spectral analysis confirmed the presence of aromatic protons (6.5–7.5 ppm) and methylene (-CH_2-) linkages (0.9–3.5 ppm) in the hydroxybenzene-methanal resins.

Materials and Methods. Nuclear Magnetic Resonance (NMR) spectroscopy is one of the analytical techniques that utilizes the nuclei of isotopes to obtain structural information about a substance. For NMR analysis, the sample is placed in a thin-walled glass tube (ampoule). When subjected to a magnetic field, NMR-active nuclei (such as ^{1}H or ^{13}C) absorb electromagnetic energy. The emitted signal's resonance frequency, energy absorption, and intensity were measured. The ^{1}H NMR spectra were recorded at a 900 MHz frequency in a 21 Tesla magnetic field.

Results and Discussion. Hydroxybenzene-methanal oligomers synthesized under different molar ratios and temperature conditions were analyzed using ^{1}H NMR spectroscopy. The chemical shifts and proton signals observed in the spectra provided insights into the structural changes of the oligomers. Significant differences were noted among the samples synthesized at different temperatures. In the ^{1}H NMR spectrum of the oligomer synthesized at 95°C, the presence of aromatic protons (6.5–7.5 ppm) and methylene (-CH_2-) groups (0.9–3.5 ppm) was clearly observed. Under this synthesis condition, strong bonding occurred between hydroxybenzene and methanal, forming a highly cross-linked structure. The sample synthesized at 80°C also showed well-defined aromatic proton and methylene group signals; however, the degree of cross-linking

appeared slightly lower than that of the high-temperature sample. Although the cross-linking remained relatively strong, the polymer chains exhibited reduced self-condensation. In the sample synthesized at 70°C, the degree of cross-linking was further reduced, but the presence of aromatic and methylene protons indicated that the aromatic structure of hydroxybenzene was preserved during synthesis. The lower synthesis temperature resulted in oligomers with less reactive but structurally stable polymer chains. These findings suggest that higher temperatures favor stronger cross-linking and polymerization, while lower temperatures lead to a more flexible and less cross-linked oligomer structure.

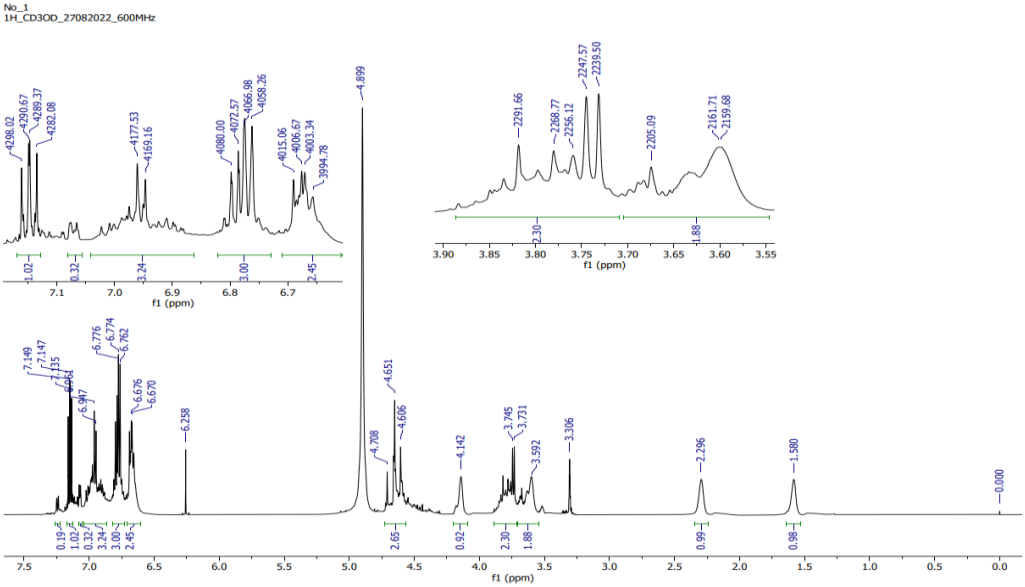

Figure 1. APEP:HMHB = 1:100 mole/mole, T = 95 °C

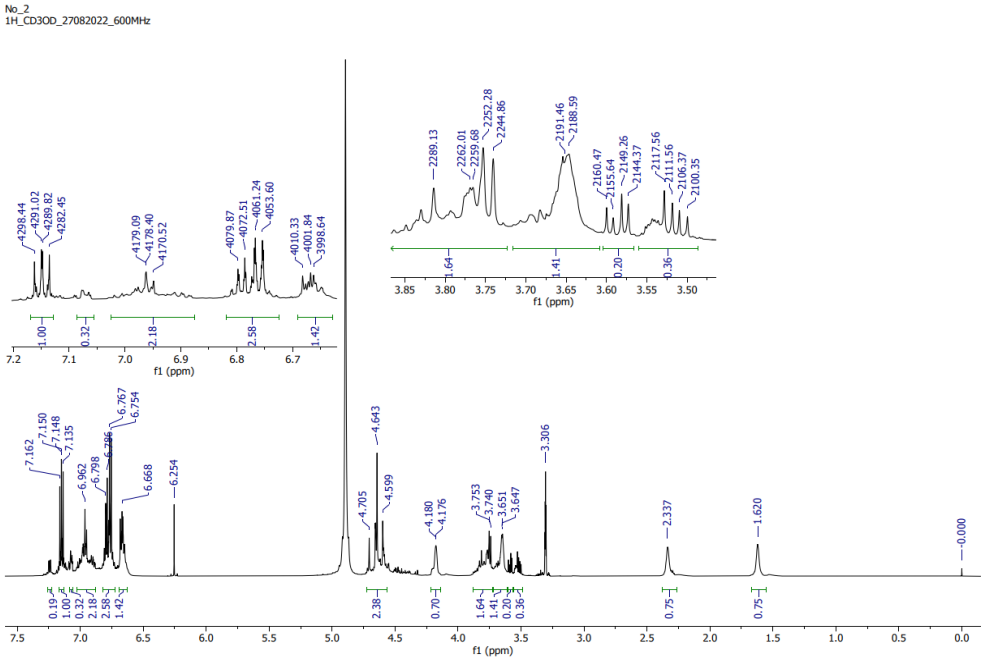

Figure 2. APEP:HMHB = 1:100 mole/mole, T = 80 °C

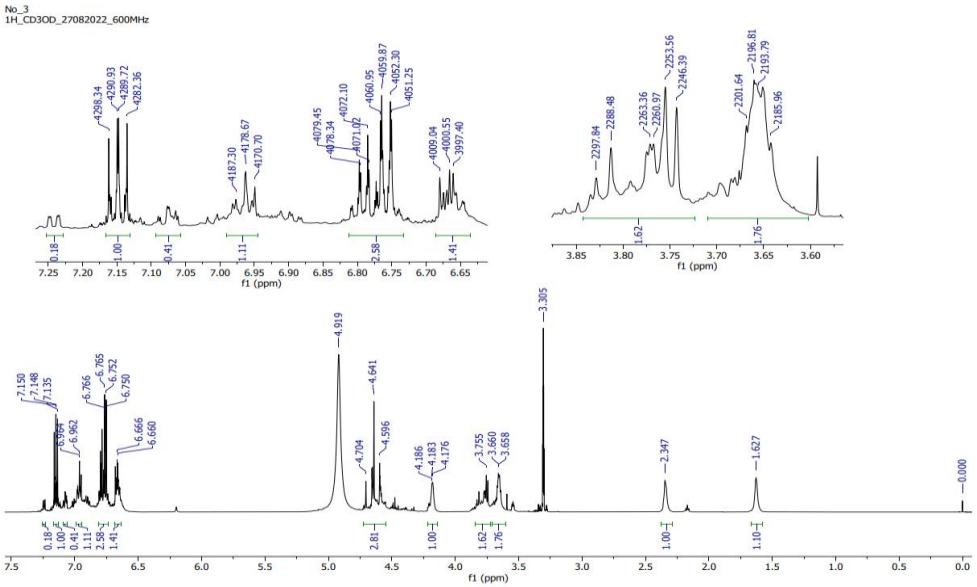

Figure 3. APEP:HMHB = 1:100 mole/mole, T = 70 °C

Samples synthesized at a 1:80 mol/mol ratio were analyzed at high (95°C, Figure 4), medium (80°C, Figure 5), and low (70°C, Figure 6) temperatures. In the sample synthesized at high temperature, strong bonding between aromatic protons and methylene groups was observed, indicating well-connected polymer chains. Under this synthesis condition, the reactions between phenol and formaldehyde proceeded to their maximum extent.

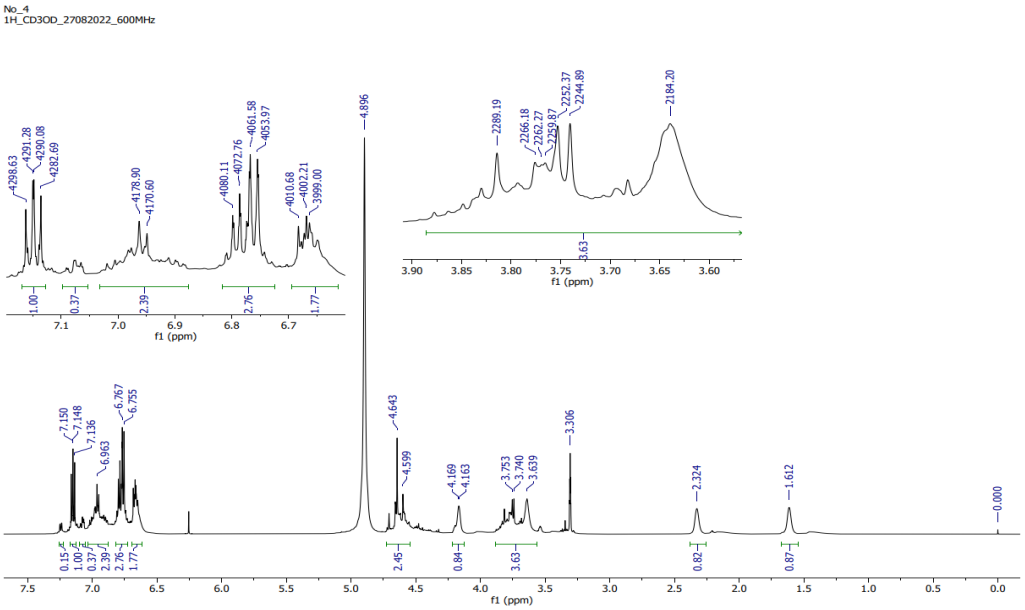

Figure 4. APEP:HMHB = 1:80 mole/mole, T = 95 °C

In the sample synthesized at 80°C, the aromatic structure of phenol and the degree of polymer chain cross-linking remained high, although the cross-linking was slightly

lower compared to the high-temperature samples. The polymers formed under this synthesis condition exhibited a well-structured and stable architecture.

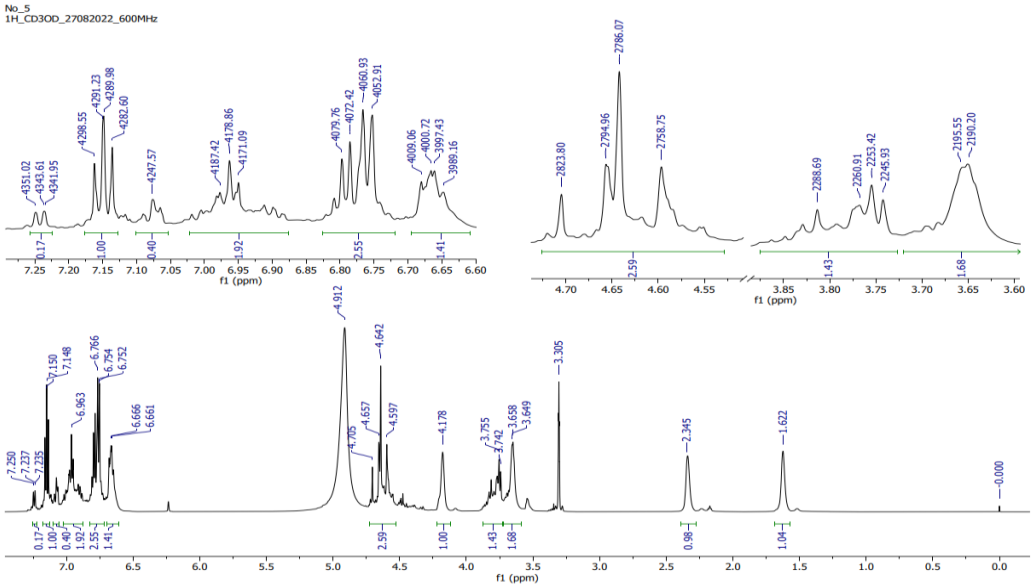

Figure 5. APEP:HMHB = 1:80 mole/mole, T = 80 °C

In the sample synthesized at 80°C, the aromatic structure of phenol and the degree of polymer chain cross-linking remained high, although the cross-linking was slightly lower compared to the high-temperature samples. The polymers formed under this synthesis condition exhibited a well-structured and stable architecture.

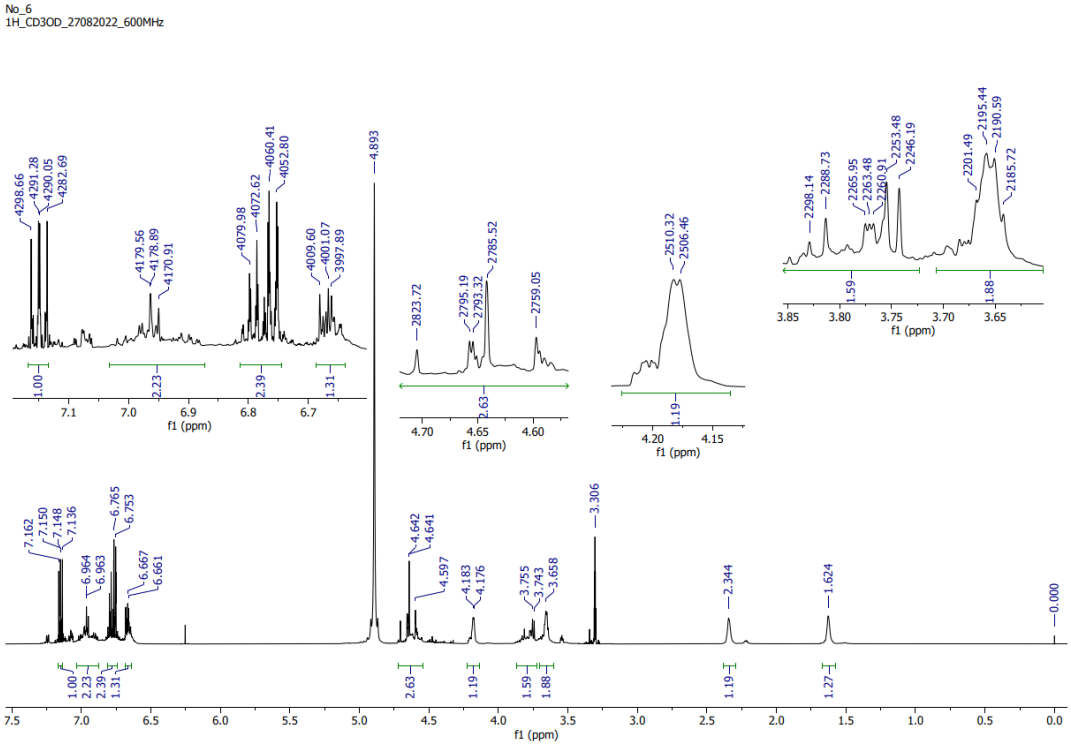

Figure 6. APEP:HMHB = 1:80 mole/mole, T = 70 °C

In the sample synthesized at 70°C, a lower degree of cross-linking was observed. Nevertheless, the presence of the aromatic structure of hydroxybenzene and methylene groups ensured the stability of the polymers formed under these conditions.

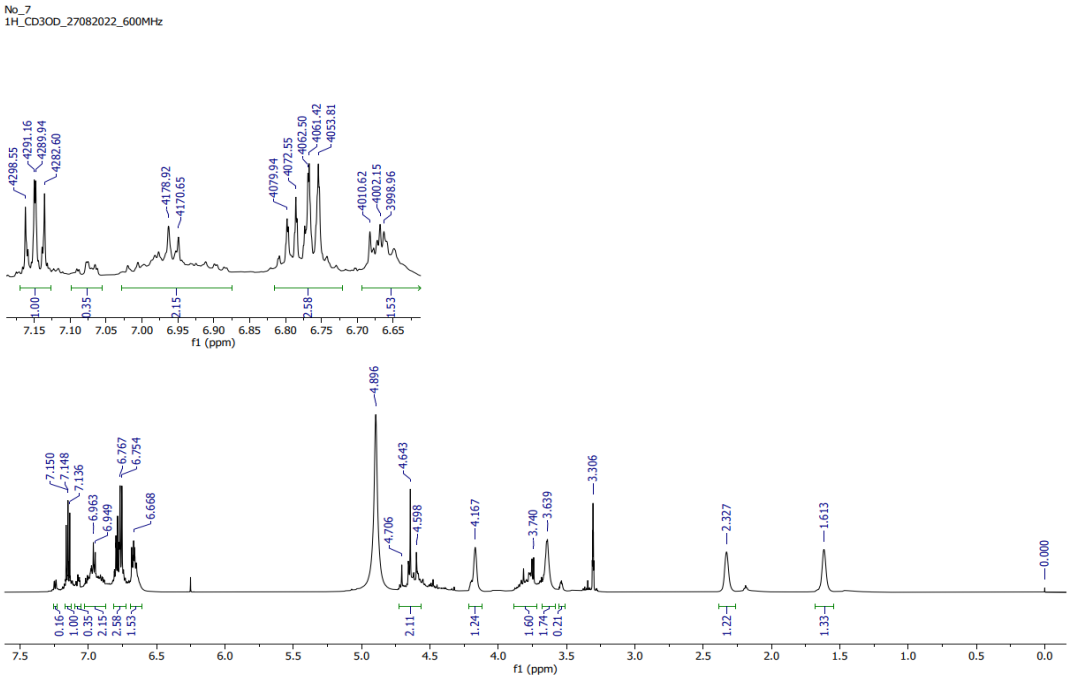

Figure 7. APEP:HMHB = 1:60 mole/mole, T = 95 °C

Oligomers synthesized at a 1:60 mol/mol ratio were analyzed at high (95 °C, Figure 7), medium (80 °C, Figure 8), and low (70 °C, Figure 9) temperatures. In the 95 °C formulation, the bonding between aromatic protons and methylene groups was strong, indicating highly cross-linked polymer chains. The oligomers formed under high-temperature conditions exhibited high stability and a well-structured architecture.

In the 80 °C formulation, the aromatic protons of hydroxybenzene and methylene groups remained intact, demonstrating well-formed polymer chains. Despite being synthesized at a lower temperature, the oligomer retained a high degree of cross-linking.

In the 70 °C formulation, a lower degree of cross-linking was observed. However, the presence of aromatic structures of hydroxybenzene and methylene groups ensured the stability of the polymers formed under these conditions.

The ^{1}H NMR results of hydroxybenzene-methanal oligomers synthesized under different ratios and temperature conditions reveal the chemical transformations occurring during the synthesis process. Overall, the analysis indicates that oligomers synthesized at higher temperatures (95°C) formed a highly cross-linked structure, ensuring greater stability and well-structured polymer chains. In contrast, those synthesized at moderate (80°C) and lower (70°C) temperatures exhibited a lower degree of cross-linking, characterized by reduced reactivity but maintained structural stability.

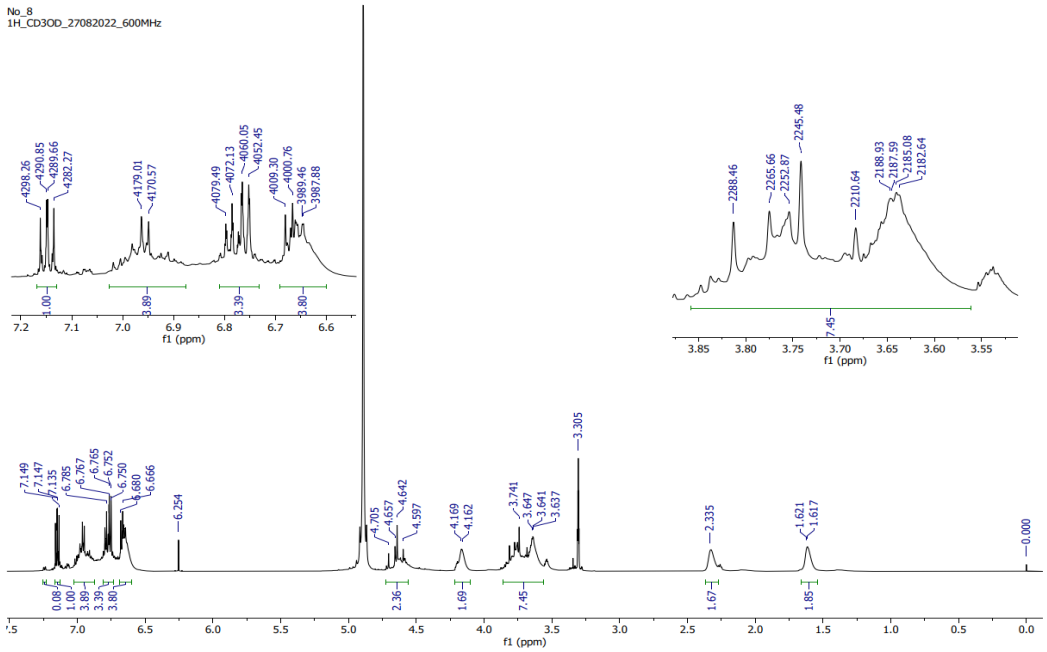

Figure 8. APEP:HMHB = 1:60 mole/mole, T = 80 °C

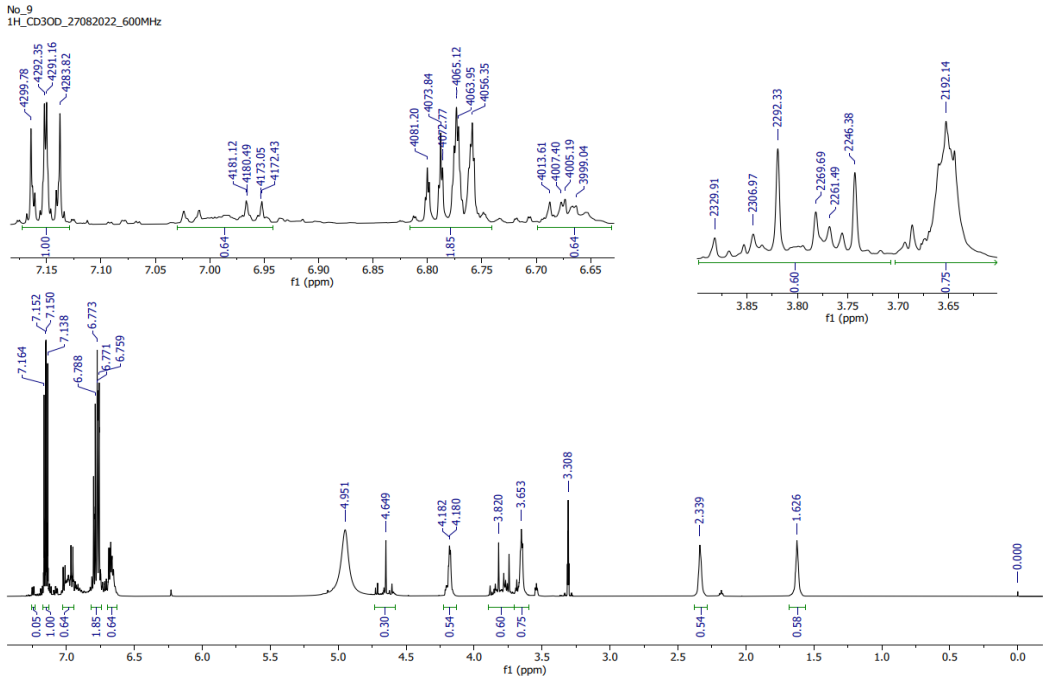

Figure 9. APEP:HMHB = 1:60 mole/mole, T = 70 °C

Conclusion. The results demonstrate that the chemical properties of the synthesized oligomers significantly vary with temperature and reactant ratio. At higher temperatures, the reaction between hydroxybenzene and methanal proceeded more efficiently, yielding highly cross-linked polymers. In contrast, at lower temperatures, the degree of cross-linking was reduced, but the structural integrity of the resulting polymers was preserved.

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