NMR SPECTROSCOPIC ANALYSIS OF THE STRUCTURE OF POLYMETHYLENENAPHTHALENESULFONIC ACID-MODIFIED POLYESTER RESIN

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Abstract: The molecular structure of polymethylenenaphthalenesulfonic acid (PMNS)-modified polyester resin synthesized from polydiethylene glycol adipinate (PDAT) and PMNS at a molar ratio of 70:1 was investigated by ^1H and ^13C NMR spectroscopy. Characteristic signals of naphthalene rings, methylene bridges, adipinate fragments, and diethylene glycol units confirmed the formation of the expected oligomeric structure. The results demonstrated the successful incorporation of PMNS into the polyester matrix and the formation of a stable modified resin system.

Keywords: polymethylenenaphthalenesulfonic acid, polydiethylene glycol adipinate, modified polyester resin, NMR spectroscopy, molecular structure, polymer modification, sulfo groups, physicochemical properties, polymer compositions.

In addition, the morphology of the synthesized samples was investigated using a **SEM-EVO MA 10** scanning electron microscope (Carl Zeiss, Germany). Prior to analysis, solid samples were thoroughly dried. Subsequently, 10–20 mg of the sample was dissolved in 0.6–0.7 mL of a deuterated solvent. The prepared solution was transferred into a standard 5 mm NMR tube. To avoid the formation of air bubbles, the solution was mixed gently and then placed in the NMR instrument for analysis [18–19].

In the initial stage of the study, nuclear magnetic resonance (NMR) spectroscopy was employed to obtain a more detailed understanding of the molecular structure of the synthesized resin. The ^1H NMR spectrum of the polyester resin prepared from polymethylenenaphthalenesulfonic acid and polydiethylene glycol adipinate at a molar ratio of 70:1 was first analyzed, and the chemical shifts corresponding to the different proton environments are presented in Figure 1.

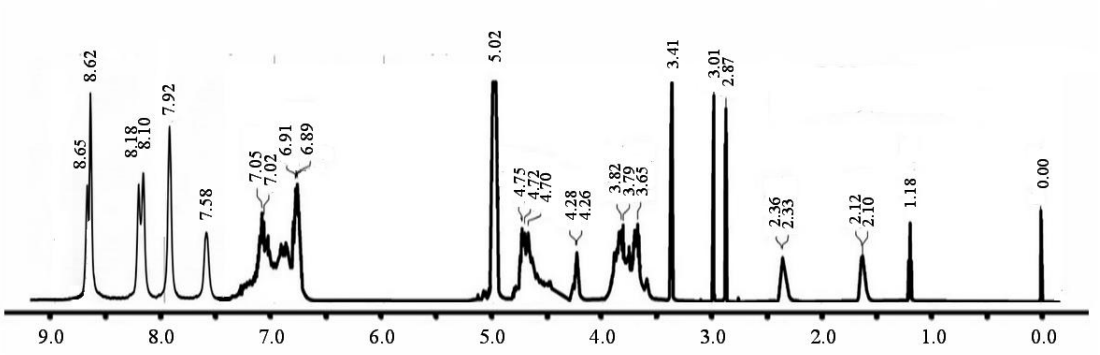

Figure 1. ^{1}H NMR spectra of the polyester resin synthesized from PMNS and PDAT at a molar ratio of 70:1.

In the above spectrum, the numerous multiplet signals observed in the region of 6.89–8.65 ppm are attributed to the aromatic protons of the naphthalene ring, confirming the preservation of the aromatic fragment within the polymer structure. Owing to the electron-withdrawing nature of the sulfo group, some aromatic protons are shifted downfield and resonate in the range of 8.0–8.7 ppm.

The intense singlet observed at 5.02 ppm is assigned to the protons of the methylene group (Ar–CH_2–O–) linking the naphthalene ring through an oxygen atom, indicating the incorporation of the aromatic fragment into the polyester chain. The signals at 4.70–4.75 ppm and around 4.26 ppm are characteristic of the methylene protons (–OCH_2–) adjacent to oxygen atoms in the diethylene glycol residue.

The multiplet signals in the range of 3.65–3.82 ppm correspond to the internal –CH_2–O–CH_2– protons of the diethylene glycol fragment. The presence of these signals confirms the formation of ether linkages within the polyester chain. The signals observed at 2.10–2.36 ppm are attributed to the methylene protons (–$COCH_2$–) adjacent to the carbonyl groups of the adipic acid residue, indicating the incorporation of the adipinate fragment into the polymer structure. The signal at 1.18 ppm corresponds to the central methylene protons of the adipic acid chain.

The simultaneous observation of signals corresponding to aromatic protons, oxygen-bonded methylene groups, and protons associated with the adipinate fragment confirms the presence of naphthalene rings, sulfo groups, and ester and ether linkages in the synthesized product. The obtained results are in good agreement with the proposed structural formula of the polyester resin modified with polymethylenenaphthalenesulfonic acid and polydiethylene glycol. Furthermore, the ^13C NMR spectrum of the same sample was investigated, and

the chemical shifts of the corresponding carbon atoms are presented in the following figure (Figure 2).

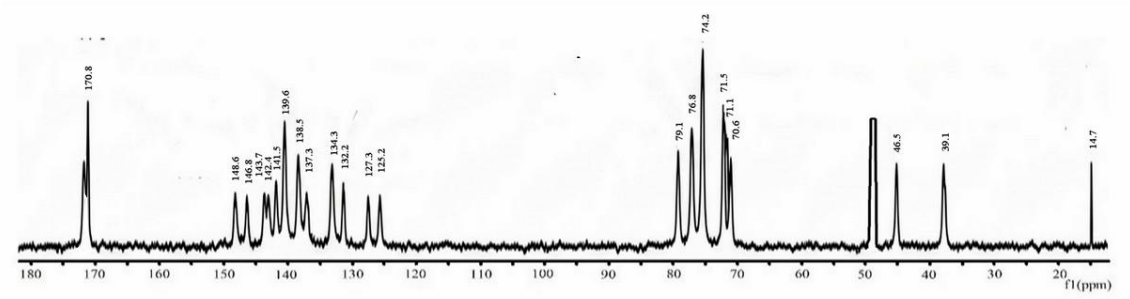

Figure 2. ^{13}C NMR spectrum of the polyester resin synthesized from PMNS and PDAT at a molar ratio of 70:1.

In the presented spectrum, the intense signal observed at 170.8 ppm is attributed to the carbonyl carbon atom of the ester group (–COO–), indicating the formation of the polyester chain. This signal confirms the presence of ester linkages formed through the condensation of adipic acid residues with diethylene glycol fragments.

The numerous resonance signals observed in the range of 149.7–125.2 ppm are assigned to the aromatic carbon atoms of the naphthalene ring. In particular, the downfield signals at approximately 149.7, 148.6, 143.7, and 141.5 ppm correspond to aromatic carbon atoms bonded to sulfo groups and oxygen-containing substituents. The resonances in the range of 139.6–125.2 ppm are attributed to the remaining aromatic carbon atoms of the naphthalene ring. The signals observed at 79.1, 76.8, 74.2, 71.5, and 70.6 ppm are characteristic of the oxygen-bonded methylene carbons (–OCH_2–) in the diethylene glycol fragment. These signals indicate the presence of polyester chains in the polymer structure and confirm the successful formation of ether linkages.

The signal observed at 46.5 ppm is assigned to the methylene carbon atom linking the naphthalene ring to the ester fragment (Ar–CH_2–O–), confirming the connection between the aromatic and aliphatic segments of the polymer. The signal at 39.1 ppm may be associated with methylene carbons located adjacent to carbonyl groups. The signal observed at 14.7 ppm is attributed to highly mobile aliphatic methylene carbons and provides additional evidence for the presence of the adipinate fragment in the synthesized polymer.

Furthermore, the presence of signals corresponding to ester carbonyl groups, the aromatic naphthalene ring, oxygen-bonded methylene carbons, and aliphatic fragments in the ^{13}C NMR spectrum confirms the existence of

naphthalene rings, sulfo groups, and ester and ether linkages in the synthesized polymer. The obtained results are in complete agreement with the proposed structural formula of the polyester resin modified with polymethylenenaphthalenesulfonic acid and polydiethylene glycol.

In general, the observation of aromatic proton and carbon signals characteristic of the naphthalene ring in the ranges of 6.89–8.65 ppm in the ^{1}H NMR spectrum and 125.2–149.7 ppm in the ^{13}C NMR spectrum confirms the presence of an aromatic fragment in the polymer structure. The intense signal at 170.8 ppm was assigned to ester carbonyl groups, whereas the signals observed in the ranges of 3.65–5.02 ppm and 70.6–79.1 ppm were attributed to the proton and carbon atoms of the $-OCH_2-$ groups in the diethylene glycol fragment. In addition, aliphatic proton and carbon signals characteristic of the adipinate fragment were detected in the regions of 1.18–2.36 ppm and 14.7–39.1 ppm, respectively. These data reliably confirm the presence of a naphthalene ring, sulfo groups, and ester and ether linkages in the synthesized product and demonstrate complete agreement with the proposed structural formula of the obtained polymer.

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