



Preparation and Characterization of a Novel Hyperbranched Polyester Polymers Using A2+B3 Monomers

Nabeel Hasan Al-Mutairi^{1*} , Ali Al-Zubiedy¹ , Ali J. Al-Zuhairi² 

¹Polymer and Petrochemical Industries Department, University of Babylon, Hilla, Iraq; nabeeleng90@gmail.com (NHA); mat.ali.alzubiedy@uobabylon.edu.iq (AJ)

²Department of Energy, College of Engineering, University of Babylon, Al-Musayyab, Iraq, alijassim33@yahoo.com

*Correspondence: nabeeleng90@gmail.com; Tel.: +9647803044501

Article history.

Received 14.07.2022

Accepted 09.12.2022

Available online 20.02.2023

Keywords

hyperbranched polyester HBP

A2+B3 monomer

polycondensation

¹H-NMR

GPC

Abstract

Compared to linear analogs, hyperbranched polymers (HBPs) have gotten much attention in the last decade because of their intrinsic globular topologies and distinctive features like low viscosity, high solubility, and a high degree of functionality. In this work, four types of hyperbranched polyester polymer HBPs have been synthesized using the A2+B3 polycondensation methodology. Firstly, the starting material B3 monomer (Pyrimidine-2,4,6-triol) has been synthesized using urea and malonic acid with the presence of sodium Na as the catalyst for the reaction. Secondly, four types of materials (tartaric acid TA, adipic acid AD, maleic acid MA, and phthalic anhydride PA) as A2 monomers were added to the starting material B3 monomer in an oil bath to prepare the four types of HBP. The chemical structure of HBPs was characterized by FTIR, and ¹H-NMR. The molecular weight of the prepared HBPs was characterized by gel permeation chromatography GPC, and thermal properties were characterized by differential scanning calorimetry DSC and thermal gravimetric analysis TGA. FTIR results showed that there are new bands, such as C-O-C between A2 and B3 monomers, as indicated by ¹H-NMR. In addition, GPC shows that the prepared polymers have a narrow molecular weight distribution with good thermal stability, as indicated by DSC and TGA.

DOI: 10.30657/pea.2023.29.5

1. Introduction

Polymers are the most commonly utilized materials in modern science and technology, and they have attracted the interest of industry and academics together. Polymers are more popular than other types of materials because of their distinct structure and properties, which have led to a wide range of applications in industries such as coatings, plastics, composites, adhesives, macromolecular building blocks, pharmaceuticals, supramolecules, and nanoscience (Mohammad, 2007).

Polymers are classified as linear, branching, or cross-linked, based on the macromolecule's structural design. Graft, comb, star, and dendritic polymers are forms of branched polymers with distinct molecular architectures. Highly branched polymers, such as hyperbranched polymers (HBP) and dendrimers, have recently been identified as a new class of polymeric materials due to their distinct physical and chemical characteristics compared to their linear analogs. When compared to their

linear analogs of similar molecular weights, highly branched dendritic polymers have many valuable properties, such as high reactivity, decreased melt and solution viscosities, a good presence of interior cavities, and so on. This is because of their globular and non-entangled structure, uniform size, high degree of branching, and multiple functional end groups. These branched polymers may be adjusted to modify the characteristics for desired applications in terms of polarity and functionality (Gao and Yan, 2004; Hobson and Harrison, 1997; Inoue, 2000; Tomalia and Fréchet, 2002).

Hyperbranched polymers are polydisperse, indefinitely branched molecules with no structural control and a high molar mass. The main advantages of hyperbranched polymers over dendrimers are that they are easier to synthesize, can be produced in one step, and provide more material at a lower cost. Flory depicted the intermolecular condensation of Abx-



© 2023 Author(s). This is an open access article licensed under the Creative Commons Attribution (CC BY) License (<https://creativecommons.org/licenses/by/4.0/>).

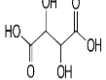
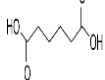
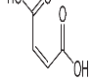

type monomers as the first hyperbranched polymer from a theoretical standpoint in 1952. In 1982, Kricheldorf reported condensation of AB and AB₂ monomers to make hyperbranched polyesters, and interest in hyperbranched polymers exploded after Kim and Webster reported the condensate of Abx-type monomers as a hyperbranched polyphenylene in 1990 (Flory, 1952; Jikei and Kakimoto, 2001; Kim and Webster, 1990; Kricheldorf et al., 1982). According to many research, dendritic polymers have been used as rheology modifiers, curing agents, dispersion agents, compatibilizers, and processing aids (Diao et al., 2006; Mulhern and Tan, 2000; Tatiya et al., 2014; Wågberg et al., 2007; Yiyun et al., 2005). In recent years, several studies have been conducted for the preparation of hyperbranched polymers that have different functional groups with different properties (AL-Abayechi et al., 2020; Al-Zuhair, 2020; Al-Zuhairi et al., 2017; Higashihara et al., 2012; Ishida et al., 2000; Yue et al., 2013; Zhang et al., 2009).

In this study, four novel hyperbranched polyester polymers have been synthesized using double monomer methodology polycondensation A₂+B₃. The starting material B₃ has been synthesized firstly, then four materials (tartaric acid TA, adipic acid AD, maleic acid MA, and phthalic anhydride PA) as A₂ monomers were added to give four types of hyperbranched polyester. These polymers were characterized using FTIR, NMR, and GPC.

2. Materials and Methods Used for the Synthesis of Hyperbranched Polyester (HBPs)

Several materials have been used for the preparation of HBPs which included pyrimidine-2,4,6-triol (C₄H₆N₂O₃) which is used as the branching agent core material (B₃ first monomer) for HBPEs and tartaric acid TA, adipic acid AD, maleic acid MA and phthalic anhydride PA used as other monomers (A₂). All the materials used in synthesizing hyperbranched Polyester polymer were obtained from Aldrich and Lancaster and used without purification. Table 1 shows the properties of these materials.

Table 1. The properties of materials used for the synthesis of HBPs

Properties	Tartaric acid	Adipic acid	Maleic acid	Phthalic anhydride
Mw (g/mol)	150.087	146.142	116.072	148.1
Density (g/cm ³)	1.79	1.36	1.59	1.53
Melting point °C	148	152.1	135	131.6
Chemical formula & structure	C ₄ H ₆ O ₆ 	C ₆ H ₁₀ O ₄ 	C ₄ H ₄ O ₄ 	C ₈ H ₄ O ₃ 

3. The Synthesis of the Starting Material (Pyrimidine-2,4,6-triol) B₃ Monomer (Figure 1)

The starting material (Pyrimidine-2,4,6-triol) used in the synthesis of the four hyperbranched polyester polymers was

prepared based on our previous work (Al-Mutairi et al., 2022). 0.5 mole (52.03 g) of malonic acid and 0.5 moles (30.03 g) of urea dissolved in 250 ml of ethanol in the presence of 11 g of sodium that was dissolved in 250 ml of ethanol in a glass beaker protected with calcium chloride. All the ingredients were mixed for 10 hours at 110 °C in the presence of molecular sieves. After the completion of the reaction, a white precipitate was formed. Then 500 ml of hot water and 45 ml of HCl were added. Then in an ice bath, the mixture was cooled for 24 hours. After that, the mixture was filtered, washed, and dried for 3 to 4 hours at a temperature of 105-110 °C. The final product is (Pyrimidine-2,4,6-triol) which was used as the starting material for the polymerization process. The overall reaction is shown in Scheme 1.

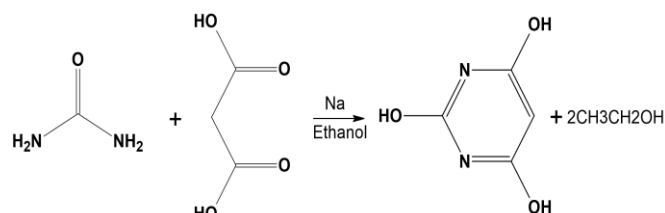


Fig. 1. The synthesis of the starting material B₃ monomer (pyrimidine-2,4,6-triol)

4. The Synthesis of Hyperbranched Polyester Polymers (Figure 2-5)

A 0.2 mol (25.6g) of the white precipitate (pyrimidine-2,4,6-triol compound) was mixed with 0.3 mol (45 g) tartaric acid TA in a round bottom flask set over an oil bath. The bath temperature was steadily increased to 170°C and then held at 160 °C for 4 hours. Continuous mixing was used until the reactants were fully melted producing a pale brown material (Hyperbranched Polyester Polymer) (AL-Abayechi et al., 2020; Al-zuhairi, 2020; Al-Zuhairi et al., 2017; Higashihara et al., 2012; Ishida et al., 2000; Yue et al., 2013; Zhang et al., 2009).

The same procedure was used for the preparation of the other three hyperbranched polymers with some difference in the number of materials and the temperature depending on the melting temperature and molecular weight of these materials as shown in Table 2. The structure and reaction between the starting material (pyrimidine-2,4,6-triol) B₃ monomer compound and the other three A₂ monomers (adipic acid AD, maleic acid MA, and phthalic anhydride PA) are shown in Figure 3 to Figure 5.

Table 2. The conditions and amount of materials used for the synthesis of HBPs

Material	B ₃ Core (g)	A ₂ Monomer (g)	Temperature (°C)	Color
HBP-TA	25.6	45	160	Pale brown
HBP-AD	25.6	44.8	170	Pale brown
HBP-MA	25.6	35.8	150	Pale yellow
HBP-PA	25.6	45	150	Pale yellow

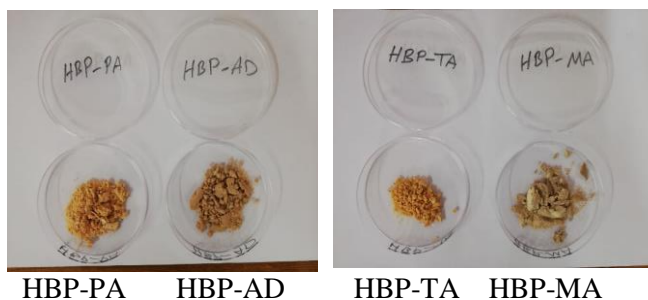


Fig. 2. The prepared hyperbranched polymers

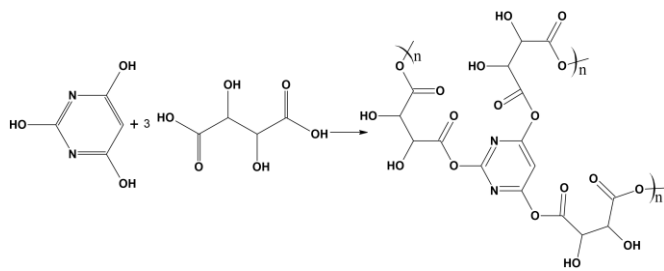


Fig. 3. The synthesis of hyperbranched polyester polymer (HBP-TA)

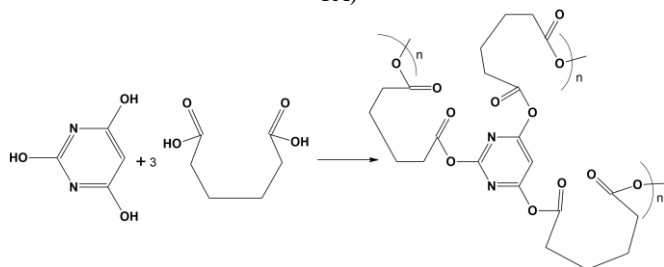


Fig. 4. The synthesis of hyperbranched polyester polymer (HBP-AD)

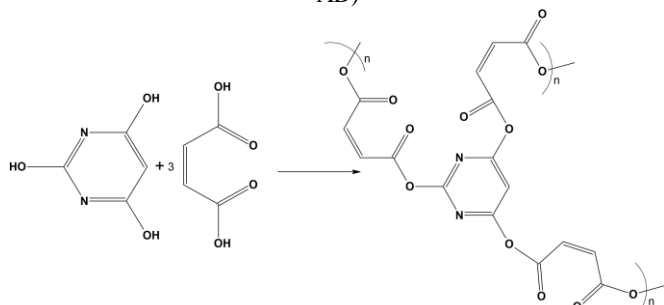


Fig. 5. The synthesis of hyperbranched polyester polymer (HBP-MA)

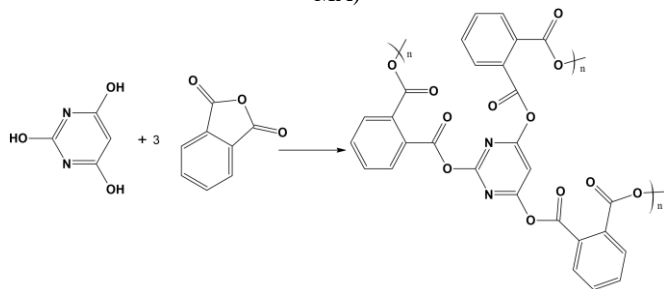


Fig. 6: The synthesis of Hyperbranched polyester polymer (HBP-PA)

5. Characterization

1. Infrared spectra (FT-IR) were measured using the FT-IR-AFinity-1 SHIMADZU range (400-4000 cm⁻¹).
2. Nuclear Magnetic analysis NMR: NMR spectra (H1-NMR): The NMR spectrum was measured using a Bruker DMX-300 NMR SPECTROPHOTOMETER 300 MHz, using DMSO-d₆ as a solvent.
3. Gel permeation chromatography (GPC; Shimadzu, Japan) with a refractive index detector was used to characterize the molecular weight of the prepared hyperbranched polyester polymers. Samples were dissolved in THF solvent at a 5 mg/mL concentration. The flow rate of the mobile phase was kept at 1.0 mL/min. The instrument was calibrated with polystyrene standards.
4. Thermal analysis: The melting points T_m of the prepared compounds were measured using the differential scanning calorimetry DSC apparatus. The samples were heated with a heating rate of 10 °C/min from 25 to 250 °C. While the thermal stability of the prepared compounds was investigated using thermogravimetric analysis TGA; the samples were heated with a heating rate of 10 °C/min from 25 to 900 °C. Both tests (DSC and TGA) were conducted under an inert gas atmosphere and with a sample weight of 10 mg±0.5.

6. Results and discussion

6.1. FTIR analysis

Figure 7 to 11 shows the FTIR spectrums of the starting material (pyrimidine-2,4,6-triol) and the four types of prepared HBP. Figure 7 shows the FTIR of the starting material, where the band values at 3332.99 cm⁻¹ and 3209.55 cm⁻¹ are for the OH group. The band at 1651.07 cm⁻¹ is for C=N and the band at 1419.81 cm⁻¹ is for Ar(C-C), and the band at 1249.87 cm⁻¹ is for C-O stretch, the band at 1157.87 cm⁻¹ is for CH wagging, and the band at 1095.57 cm⁻¹ is for C-O stretch (R₂CHOH). The band at 995.27 cm⁻¹ is for (=CH) out of a plane. The bands at 740.67 and 702.09 are for (N-H) and (C-H) out of a plane.

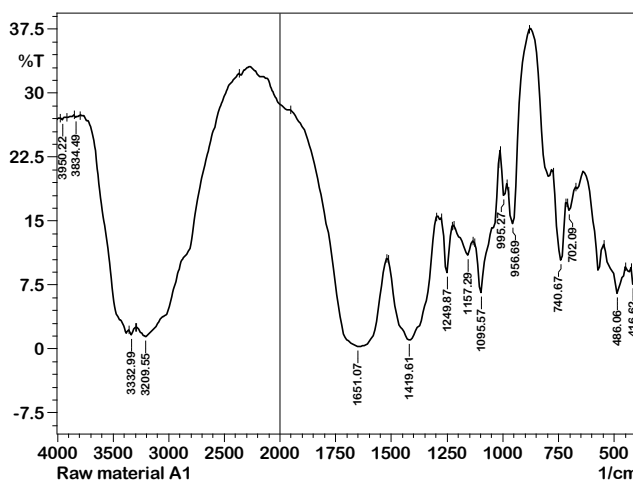


Fig. 7. FTIR of pyrimidine-2,4,6-triol (starting material) B3 monomer

Figure 8 shows the FTIR spectrum of HBP-TA, where the band values at 3410.15 cm^{-1} and 3224.98 cm^{-1} for O-H stretch, and the band at 3101.54 cm^{-1} for OH dimer. The band at 2877.79 cm^{-1} is for the CH stretch, and the band at 1712.79 cm^{-1} is for C=O, while the band at 1419.61 is for Ar (C-C) stretch. Also, the band is at 1365.60 cm^{-1} and 1350.17 cm^{-1} for C-H rocking. While the band at 1249.87 cm^{-1} is for C-O stretch esters (RCOOR'), and the band at 1195.87 cm^{-1} is for -C-O stretch phenol Ar(OH). The band at 1134.14 cm^{-1} is for C-O-C stretch and the band at 1087.85 cm^{-1} is for C-O stretch, and the band at 1033 cm^{-1} is for C-O stretch (R2NH), while the bands at 802.39 cm^{-1} and 771.53 cm^{-1} are for CH out of a plane (Ar tri-sub.) and the band at 732.95 cm^{-1} for C-H out of a plane (Ar mono-sub.), and the bands at 663.51 cm^{-1} and 632.65 cm^{-1} are for C-H bend.

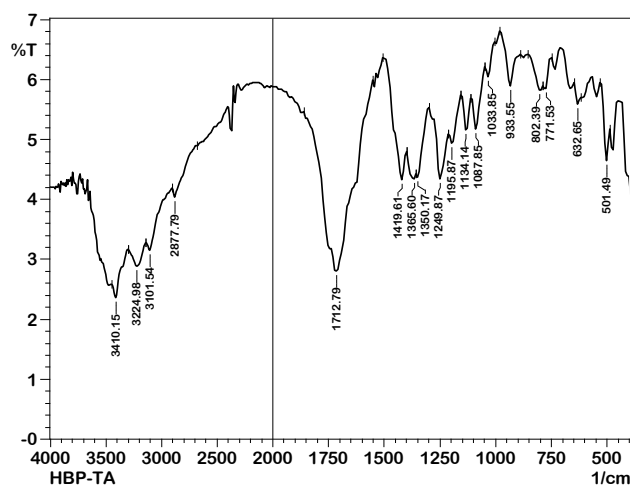


Fig. 8. FTIR of Hyperbranched Polyester Polymer with Tartaric acid HBP-TA

Figure 9 shows the FTIR spectrum of HBP-AD, where the band at 3479.58 cm^{-1} is for OH stretch, and the bands at 3186.4 cm^{-1} and 3101.54 cm^{-1} are for OH dimer. While the band at 2962.66 cm^{-1} is for CH_3 stretch and the band at 2877.79 cm^{-1} is for CH stretch. The band at 1697.36 cm^{-1} is for the C=O stretch, and the band at 1419.61 cm^{-1} is for Ar(C-C) stretch. In addition, the band at 1350.17 cm^{-1} is for C-H rocking, the band at 1280.73 cm^{-1} is for C-N stretch, 1195.87 cm^{-1} is for -C-O stretch and the band at 1033.85 cm^{-1} is for C-O stretch. The other bands at 925.83 cm^{-1} for O-H bend (RCOOH), and the bands at 771.53 cm^{-1} are for CH out of a plane (Ar tri-sub.) and at 732.95 cm^{-1} for C-H out of a plane (Ar mono-sub.), the band at 686.66 cm^{-1} is for =CH out of the plane, and the band at 632.65 cm^{-1} is for C-H bend.

Figure 10 shows the FTIR spectrum of HBP-MA, where the bands at 3479.58 cm^{-1} and 3417.89 cm^{-1} are for OH stretch, and the bands at 3201.83 cm^{-1} and 3062.96 cm^{-1} are for OH dimer. While the band at 2877.79 cm^{-1} for CH stretch, and the band at 1705.07 cm^{-1} for C=O stretch. The band at 1635.64 cm^{-1} for N-H bends out of the plane. The bands at 1589.34 cm^{-1} and 1427.32 cm^{-1} are for Ar. (C-C) stretch. In addition, the band at 1373.32 cm^{-1} is for R-CH, the bands at 1257.59 cm^{-1} are for C-N stretch, and the band at 1033.85 cm^{-1} is for C-O stretch is for esters, while the band at 933.11 cm^{-1} is for OH

bend of RCOOH. The other bands at 864.11 cm^{-1} and 779.24 cm^{-1} are for Ar. C-H out of a plane, and bands at 632.65 cm^{-1} and 609.51 cm^{-1} for C-H bend.

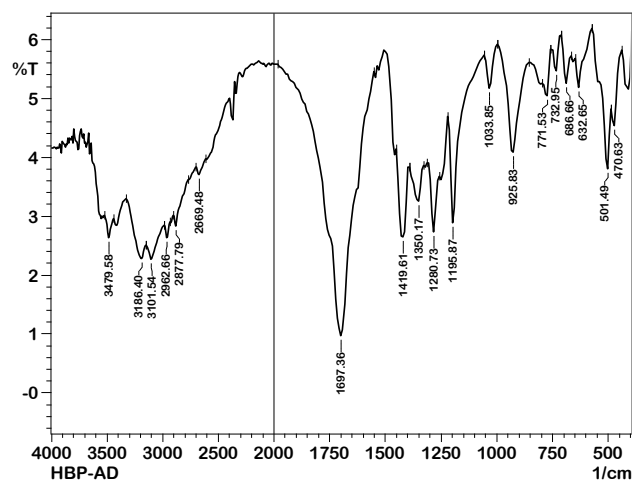


Fig. 9. FTIR of Hyperbranched Polyester Polymer with Adipic acid HBP-AD

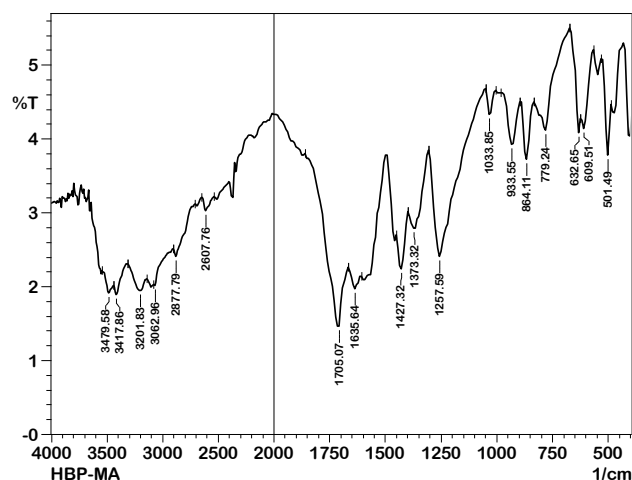


Fig. 10. FTIR of Hyperbranched Polyester Polymer with Maleic acid HBP-MA

Figure 11 shows the FTIR spectrum of HBP-PA, where the band at 3479.58 cm^{-1} is for O-H stretch, and the band at 3194.12 cm^{-1} and at 3101.54 cm^{-1} for OH dimer. While the band at 2877.79 cm^{-1} is for CH stretch, and the band at 1759.08 cm^{-1} is for C=O stretch symmetric (anhydrides RCO-O-COR'). In addition, the band at 1697.36 cm^{-1} is for C=N, and the band at 1411.89 cm^{-1} is for Ar(C-C) stretch, while the band at 1350.17 cm^{-1} is for C-H rocking. Also, the band at 1257.59 cm^{-1} is for esters C-O stretch (RCOOR'), the band at 1111.89 cm^{-1} is for C-O-C stretch, and the bands at 1072.42 cm^{-1} and 1033 cm^{-1} are for C-O stretch. The other bands at 910.40 cm^{-1} and 794.67 cm^{-1} for =CH out of the plane, and the bands at 740.67 cm^{-1} and 709.80 cm^{-1} for Ar (C-H) out of the plane, while the bands at 671.23 cm^{-1} and 632.65 cm^{-1} for C-H bend.

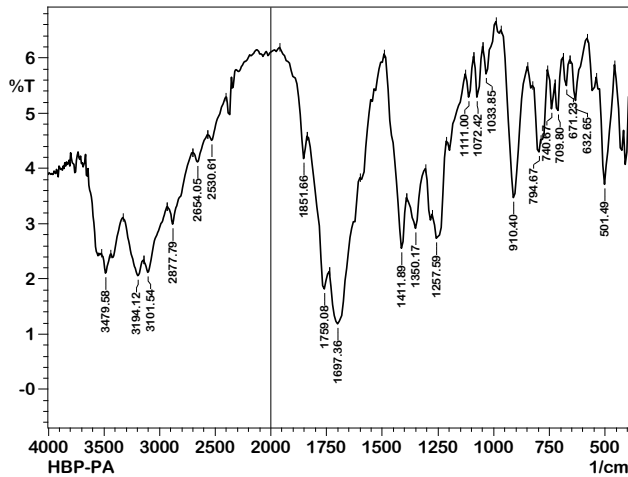


Fig. 11. FTIR of Hyperbranched Polyester Polymer with Phthalic anhydride HBP-PA

6.2. NMR analysis

To further confirm the chemical structure of the starting material (pyrimidine-2,4,6-triol) and the four types of the prepared HBP, the ¹H-NMR measurements were performed. The data of ¹H-NMR confirmed the structure of the raw material (pyrimidine-2,4,6-triol) and HBP polymers.

Figure 12 shows the ¹H-NMR of pyrimidine-2,4,6-triol, it shows that the DMSO-d₆ signal was seen at 2.4 ppm. The signals at 4.162-4.315 ppm attributed to (S, 1H, CH pyrimidine), the signal at 8.499 ppm (S, 1H, imidic OH), and the signal at 10.165 ppm related to (S, 1H, phenolic OH).

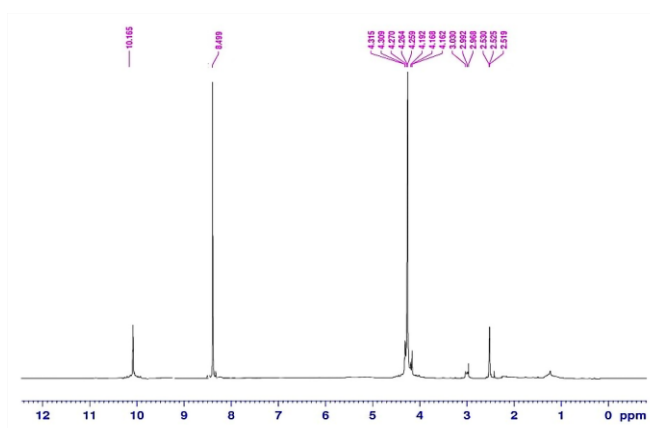


Fig. 12. ¹H-NMR of pyrimidine-2,4,6-triol (starting material) B3 monomer

Figure 13 shows the ¹H-NMR of Hyperbranched polyester polymer with tartaric acid (HBP-TA), it's found that the signal at 4.082 ppm related to (S, 1H, CH pyrimidine), the signals at 3.062-3.082 ppm related to (d, 6H, OH tartaric group), and the signal at 5.153 ppm attributed to (d, 6H, CH tartaric group).

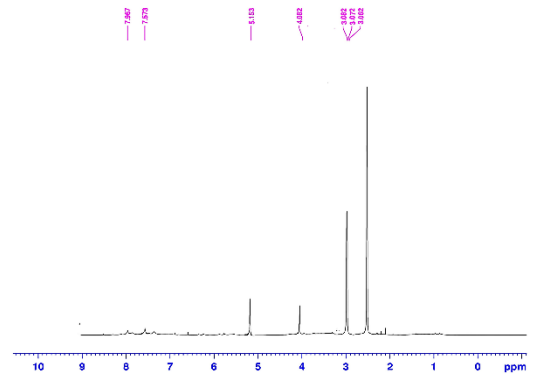


Fig. 13. ¹H-NMR of Hyperbranched Polyester Polymer with Tartaric acid HBP-TA

Figure 14 shows the ¹H-NMR of Hyperbranched polyester polymer with adipic acid (HBP-AD), it's found that the signals at 3.965-4.091 ppm for (S, 1H, CH pyrimidine), the signals at 1.649-1.689 ppm related to (t, 12H, CH₂ adipic group) the signals at 2.016-2.033 ppm for (t, 12H, CH₂ adipic group).

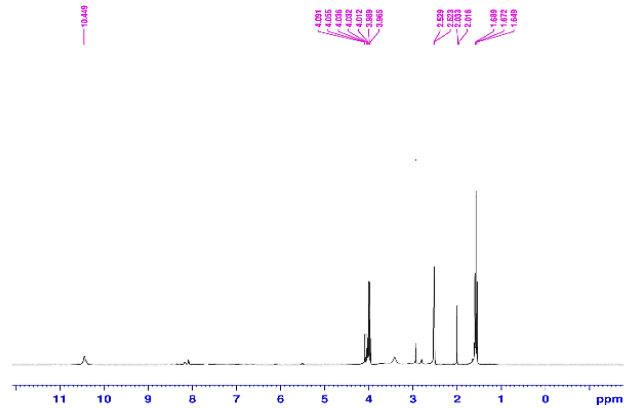


Fig. 14. ¹H-NMR of Hyperbranched Polyester Polymer with Adipic acid HBP-AD

Figure 15 shows the ¹H-NMR of Hyperbranched polyester polymer with Maleic acid (HBP-MA), it's found that the signal at 4.052 ppm for (S, 1H, CH pyrimidine), the signals from 6.504-6.514 ppm for (d, 3H, malic acid (trans)), and the signals from 6.661-6.663 ppm for (d, 6H, malic acid (cis)).

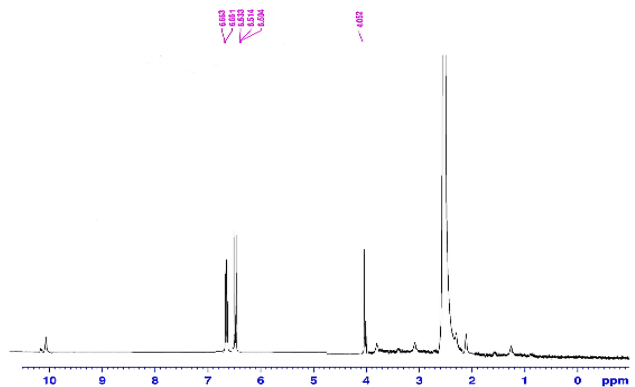


Fig. 15. ¹H-NMR of Hyperbranched Polyester Polymer with Maleic acid HBP-MA

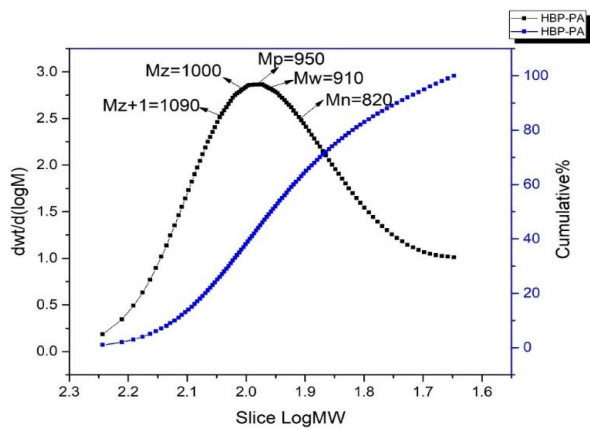


Fig. 20. GPC curve of HBP-PA polymer

Table 3. The GPC data for the prepared polymers

Material	Mn	Mw	Mp	PDI
HBP-TA	870	1140	1130	1.303
HBP-AD	890	1120	1040	1.258
HBP-MA	1705	1880	1875	1.185
HBP-PA	850	910	950	1.109

All the data are in (g/mol) except PDI has no units.

6.4. Thermal analysis results

Figure 21 shows the melting temperature of the prepared HBP. It's found that the melting temperature of HBP-TA is 168.81 °C, of HBP-AD is 155.49 °C, HBP-MA is 148.27 °C, and HBP-PA is 197.49 °C. From these results, it is found that the HBP-PA has the highest melting temperature over the other prepared polymers due to the presence of aromatic rings in its structure, while HBP-TA and HBP-AD have lower melting temperatures than HBP-PA, due to the presence of hydroxyl groups in HBP-TA and CH₂ in the main chain of HBP-AD. While HBP-MA has the lowest melting temperature of the four polymers, also it is shown in Table 3) that the melting enthalpy ΔH_m of the prepared polymers is related to melting temperature, this may be due to the short chains and the lower functional groups (OH) within its structure.

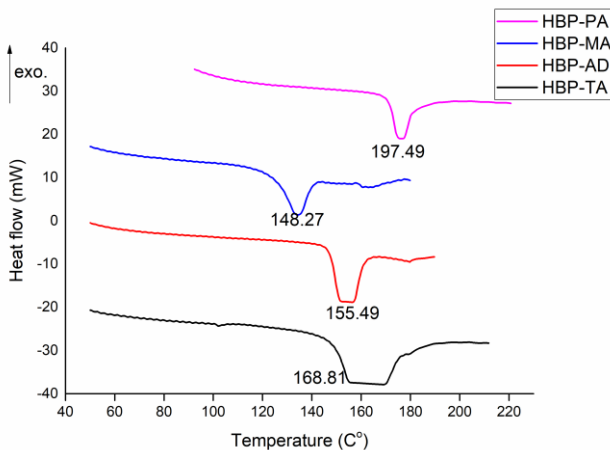


Fig. 21. DSC curves of the prepared HBP polymers

Table 4. DSC data for the prepared HBPs.

Samples	T _m (°C)	ΔH _m (J/g)
HBP-TA	168.81	123.72
HBP-AD	155.49	81.97
HBP-MA	148.27	56.49
HBP-PA	197.49	95.22

The thermal stability of a polymer can provide important guidance for its processing and application. The studies of thermal behavior not only can explain the behavior of a polymer at high temperatures but also assist in the establishment of selection criteria for specific applications of polymer materials.

Figure 22 shows the TGA and DTG curves for the prepared HBP. It was found that both HBP-TA and HBP-AD showed a two-stage degradation process, while HBP-MA and HBP-PA showed three stage degradation process. For HBP-TA the first stage degradation starts between 201 to 276°C with 49.5% weight loss and the second stage degradation starts between 285 to 584°C with 27.9% weight loss, while for HBP-AD the first stage start between 131 to 338°C with 64.6% weight loss and the second stage degradation start between 347 to 597°C with 24.3% weight loss. The research results revealed that HBP-TA has better thermal stability than HBP-AD because HBP-TA has a higher molecular weight than HBP-AD and also has higher OH content and lower branch length.

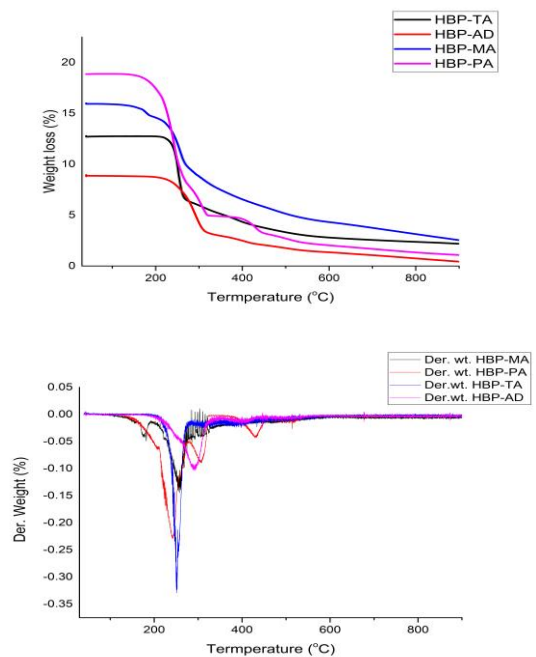


Fig. 22. TGA and DTA curves for the prepared HBP

For HBP-MA the first stage degradation process starts between 104 to 176°C with 7.2% weight loss, the second stage degradation process start between 193 to 289°C with 32.6% weight loss, and the third stage degradation process starts between 292 to 595°C with 25.9% weight loss. While, for HBP-PA the first stage degradation process starts between 113 to

319°C with 73.42% weight loss, the second stage start between 328 to 452°C with 9.4% weight loss, and the third stage start between 465 to 581°C with 9.61 weight loss. From these results, it's found that the HBP-PA has better thermal stability than HBP-MA which may be attributed to the presence of an aromatic ring within its structure, and also to the higher melting enthalpy as indicated by Table 4.

5. Conclusion

From the above results, it is found that FTIR analysis shows that each of the four types of HBP has various functional groups within the same macromolecule such as OH, C-N, C=O, C-O, and C-O-C while ¹H-NMR shows the interaction and bonding between these groups (groups with Hydrogen). GPC shows that three of the four prepared HBP polymers (HBP-TA, HBP-AD, and HBP-PA) have narrow molecular weight and polydispersity index PDI except HBP-MA has a higher molecular weight. DSC shows that each of the prepared HBP polymers has different melting temperature due to the difference in their chemical structure, HBP-PA has the highest melting temperature due to the presence of an aromatic ring in its structure. TGA showed that HBP-TA and HBP-AD polymers have two stages of thermal degradation, while HBP-MA and HBP-PA have three stages of thermal degradation, and it is found that all the HBP polymers have good thermal stability.

Acknowledgments

The cooperation of the laboratory staff at the department of polymer and petrochemical engineering is appreciated.

Reference

AL-Abayechi, M.M.H., AL-Zuhairi, A.J., AL-Baiati, M.N., 2020. Physical properties of hyperbranched polymers containing melamine derivative. *AIP Conference Proceedings*, 2290(1), 30027.

Al-Mutairi, N.H., Al-Zubiedy, A., J Al-Zuhairi, A., 2022. Hyperbranched Polyester Polymer Preparation and Study Its Effect on Some Properties of Polypropylene. *Egyptian Journal of Chemistry*, 65(8), 35–43.

Al-zuhairi, A., 2020. Synthesis of Hyper Branched Polyester Polymers Containing Thiobarbituric Acid and Study of its Optical Properties. 12(1), 1–11.

Al-Zuhairi, A.J., Allw, A.S., Obaid, K.A., Rasool, S.R., Mousa, A.O., 2017. Synthesis of hyperbranched polymers and study of its optical properties. *Journal of Engineering and Applied Sciences*, 12(Specialissue6), 7800–7804. DOI: 10.3923/jeasci.2017.7800.7804

Diao, J., Song, X., PENG, Z. H., Wang, Y., 2006. Compatibilization effects of a hyperbranched polymer on acrylonitrile-butadiene-styrene/poly(vinylchloride) blends. *Iranian Polymer Journal (English)*, 15(11), 863–870.

Flory, P. J., 1952. Molecular size distribution in three dimensional polymers. VI. Branched polymers containing A—R—Bf-1 type units. *Journal of the American Chemical Society*, 74(11), 2718–2723.

Gao, C., Yan, D., 2004. Hyperbranched polymers: From synthesis to applications. *Progress in Polymer Science (Oxford)*, 29(3), 183–275. DOI: 10.1016/j.progpolymsci.2003.12.002

Higashihara, T., Segawa, Y., Sinananwanich, W., Ueda, M., 2012. Synthesis of hyperbranched polymers with controlled degree of branching. *Polymer Journal*, 44(1), 14–29. DOI: 10.1038/pj.2011.99

Hobson, L.J., Harrison, R.M., 1997. Dendritic and hyperbranched polymers: advances in synthesis and applications. *Current Opinion in Solid State and Materials Science*, 2(6), 683–692.

Inoue, K., 2000. Functional dendrimers, hyperbranched and star polymers. *Progress in Polymer Science*, 25(4), 453–571.

Ishida, Y., Jikei, M., Kakimoto, M.A., 2000. Synthesis of hyperbranched aromatic polyesters by carbon monoxide insertion reaction using palladium catalyst. *Polymers for Advanced Technologies*, 11(8–12), 698–704. DOI: 10.1002/1099-1581(200008/12)11:8/12<698::AID-PAT22>3.0.CO;2-W

Jikei, M., Kakimoto, M., 2001. Hyperbranched polymers: a promising new class of materials. *Progress in Polymer Science*, 26(8), 1233–1285.

Kim, Y.H., Webster, O.W., 1990. Water soluble hyperbranched polyphenylene: "a unimolecular micelle?". *Journal of the American Chemical Society*, 112(11), 4592–4593.

Kricheldorf, H.R., Zang, Q.Z., Schwarz, G., 1982. New polymer syntheses: 6. Linear and branched poly (3-hydroxy-benzoates). *Polymer*, 23(12), 1821–1829.

Mohammad, F., 2007. Specialty polymers: materials and applications. IK International Pvt Ltd.

Mulkern, T.J., Tan, N.C.B., 2000. Processing and characterization of reactive polystyrene/hyperbranched polyester blends. *Polymer*, 41(9), 3193–3203.

Tatiya, P.D., Nevare, M.R., Mahulikar, P.P., Gite, V.V., 2014. Melt processing and characterization of nanocomposites of PP/Na+ MMT blending with hyperbranched polyester. *Polymer-Plastics Technology and Engineering*, 53(9), 941–951.

Tomalia, D.A., Fréchet, J.M.J., 2002. Discovery of dendrimers and dendritic polymers: a brief historical perspective. *Journal of Polymer Science Part A: Polymer Chemistry*, 40(16), 2719–2728.

Wågberg, L., Ondaral, S., Enarsson, L.E., 2007. Hyperbranched polymers as a fixing agent for dissolved and colloidal substances on fiber and SiO₂ surfaces. *Industrial & Engineering Chemistry Research*, 46(7), 2212–2219.

Yiyun, C., Dazhu, C., Rongqiang, F., Pingsheng, H., 2005. Behavior of polyamidoamine dendrimers as curing agents in bis-phenol A epoxy resin systems. *Polymer International*, 54(3), 495–499.

Yue, L., Cao, Y., Huang, T., Huang, L., Bai, Y., Zhou, Y., 2013. Synthesis of aromatic hyperbranched polyester (HBPE) and its use as a nonmigrating plasticiser. *Australian Journal of Chemistry*, 67(1), 22–30.

Zhang, D., Jia, D., Zhou, Z., 2009. Synthesis and characterization of low viscosity aromatic hyperbranched polyester epoxy resin. *Macromolecular Research*, 17(5), 289–295. <https://doi.org/10.1007/BF03218864>

使用 A2+B3 单体制备和表征新型超支化聚酯聚合物

關鍵詞

超支化聚酯
HBP
A2+B3单体
缩聚
¹H-NMR
GPC

摘要

与线性类似物相比，超支化聚合物（HBP）在过去十年中因其固有的球状拓扑结构和低粘度、高溶解度和高功能度等显著特征而受到广泛关注。在这项工作中，使用 A2+B3 缩聚方法合成了四种类型的超支化聚酯聚合物 HBP。首先，在钠钠作为反应催化剂的情况下，使用尿素和丙二酸合成了起始原料 B3 单体（嘧啶-2,4,6-三醇）。其次，在油浴中将四种物质（焦油-酒石酸TA、己二酸AD、马来酸MA和邻苯二甲酸酐PA）作为A2单体加入到起始原料B3单体中，制备四种HBP。HBPs 的化学结构通过 FTIR 和 ¹H-NMR 表征。制备的HBPs的分子量采用凝胶渗透色谱GPC表征，热性能采用差示扫描量热DSC和热重分析TGA表征。FTIR结果表明，如¹H-NMR所示，A2和B3单体之间存在新的条带，例如C-O-C。此外，GPC 表明制备的聚合物具有窄的分子量分布和良好的热稳定性，如 DSC 和 TGA 所示。
