



Research Article

Comparative Study of Synthesis Characterization and Thermal Properties of Homomer and Copolymers of N-Benzylmaleimide

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Abstract

N-Benzylmaleimide (NBMI) was synthesized and subsequently copolymerized with methyl methacrylate (MMA) through free-radical polymerization in tetrahydrofuran (THF), using azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) as initiators. The synthesized NBMI homopolymer and NBMI-MMA copolymer (CBMI) were characterized by Fourier-transform infrared (FT-IR) spectroscopy, proton nuclear magnetic resonance (¹H NMR) spectroscopy, solubility studies, intrinsic-viscosity measurements, gel permeation chromatography (GPC), and thermogravimetric analysis (TGA). The NBMI homopolymer and CBMI copolymer were obtained in yields of 39.5% and 44.0%, respectively, with intrinsic-viscosity values of 0.031 and 0.060 dL/g. FT-IR and ¹H NMR analyses confirmed the consumption of the maleimide carbon–carbon double bond during polymerization, while the characteristic imide-ring structure remained intact. Solubility studies revealed that the CBMI copolymer exhibited favourable solubility in several organic solvents. GPC analysis showed that the copolymer possessed a molecular weight of 25,881 g mol⁻¹. Furthermore, TGA demonstrated a predominantly single-stage degradation pattern and satisfactory thermal stability. The higher yield and intrinsic viscosity of CBMI compared with the NBMI homopolymer indicate the successful incorporation of MMA into the polymer system. Overall, the results demonstrate that NBMI-MMA copolymer exhibits favourable structural, physicochemical, and thermal characteristics, making it a promising material for potential advanced polymer applications.

Keywords

N-Benzylmaleimide, Methyl Methacrylate, NBMI-MMA Copolymer, Free-radical Copolymerization, Thermogravimetric Analysis, Thermal Stability

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1. Introduction

Maleimides readily participate in copolymerization reactions with a wide range of vinyl monomers, enabling the preparation of structurally modified vinyl polymers with improved performance. Incorporation of the imide ring into the polymer backbone contributes substantially to the thermal and mechanical properties of the resulting materials [1-3]. Consequently, polymaleimides are recognized as an important category of high-performance polymers [4], exhibiting excellent mechanical strength and thermal stability because of the rigid cyclic imide functionality present within their molecular structure [5].

N-substituted maleimides are particularly valuable monomers for the development of thermoplastic polymeric materials. Their incorporation into polymer chains can considerably enhance chemical stability, heat resistance, and resistance to organic solvents [6]. During free-radical copolymerization, maleimide units restrict segmental chain mobility, resulting in increased thermal stability and glass-transition temperature. These monomers also provide an effective route for introducing different functional groups into vinyl polymer backbones in a controlled manner. In the presence of suitable radical initiators, N-substituted maleimides undergo polymerization to produce materials with improved mechanical performance and resistance to thermal degradation [7-14].

Previous investigations have examined the homopolymerization and copolymerization behaviour of N-benzylmaleimide (NBMI) using benzoyl peroxide (BPO) as a free-radical initiator in different reaction media at 65 °C [15, 16]. In the present investigation, NBMI was copolymerized with methyl methacrylate (MMA) through free-radical polymerization. The resulting copolymers were subjected to spectroscopic, thermal, and physicochemical characterization to establish their chemical structures and evaluate their material properties.

In related studies, the p-NPAM monomer was synthesized and subsequently copolymerized with MMA in tetrahydrofuran (THF), using azobisisobutyronitrile (AIBN) as the free-radical initiator. The chemical structures of the monomer and its corresponding copolymer were verified through Fourier-transform infrared (FT-IR) and proton nuclear magnetic resonance (¹H NMR) spectroscopy. Their physicochemical properties were assessed through solubility testing and intrinsic-viscosity measurements. Thermogravimetric analysis (TGA)

was employed to investigate thermal behaviour, while gel permeation chromatography (GPC) was used to determine the molecular-weight characteristics of the synthesized polymers [17, 18].

2. Experimental Work

N-Benzylmaleimide (NBMI) is synthesized and subsequently copolymerized with methyl methacrylate (MMA) through a free-radical polymerization process.

2.1. Materials

Maleic anhydride and N-benzylmaleimide (NBMI) were purified by recrystallization from acetone. The hydroquinone inhibitor present in methyl methacrylate (MMA) was removed by washing the monomer two to three times with a 5% sodium hydroxide solution. The purified MMA was subsequently dried over anhydrous calcium chloride (CaCl₂) for five hours and redistilled before use. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol, whereas benzoyl peroxide (BPO) was used as supplied without further purification. Dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and 1,4-dioxane were purified by distillation. Analytical-grade N, N-dimethylformamide (DMF) and methanol were used as received.

2.2. Methods

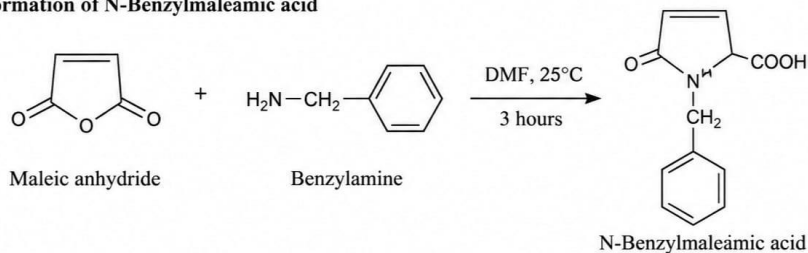
NBMI was synthesized from maleic anhydride and benzylamine via a two-step process.

2.2.1. Synthesis of N-Benzylmaleamic acid (NBMA)

A solution of maleic anhydride (20.6 g, 0.2 mol) in N, N-dimethylformamide (DMF) was added gradually over 10 min to a continuously stirred solution of benzylamine (32.3 g, 0.2 mol). The reaction mixture was maintained at room temperature with constant stirring for 3 h and subsequently poured onto crushed ice, resulting in the precipitation of crude N-benzylmaleamic acid (NBMA). The isolated product was purified by recrystallization from ethanol.

2.2.2. Synthesis of N-Benzylmaleimide (NBMI)

Step 1: Formation of N-Benzylmaleamic acid



Step 2: Cyclodehydration to N-Benzylmaleimide

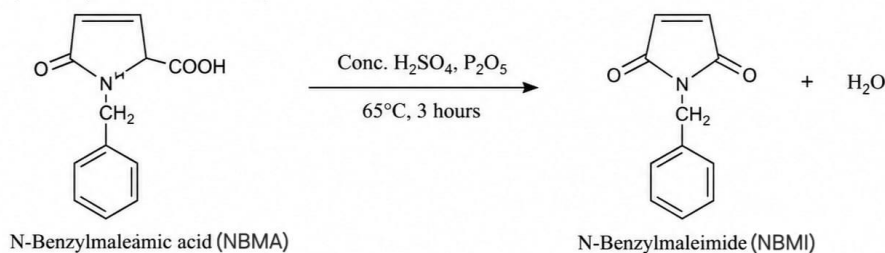


Figure 1. Synthesis of Monomer N-Benzylmaleimide [17].

N-Benzylmaleamic acid (NBMA) was dissolved in N, N-dimethylformamide (DMF) at 25 °C. A DMF solution containing sulfuric acid (H₂SO₄) and phosphorus pentoxide (P₂O₅) was then introduced as the cyclodehydration reagent. The resulting reaction mixture was continuously stirred at 65 °C for 3 h to facilitate conversion of NBMA into the corresponding

maleimide. After cooling to room temperature, the mixture was transferred onto crushed ice, leading to precipitation of the crude product. The isolated material was subsequently recrystallized from 1,4-dioxane to obtain purified N-benzylmaleimide (NBMI).

2.3. Copolymerization

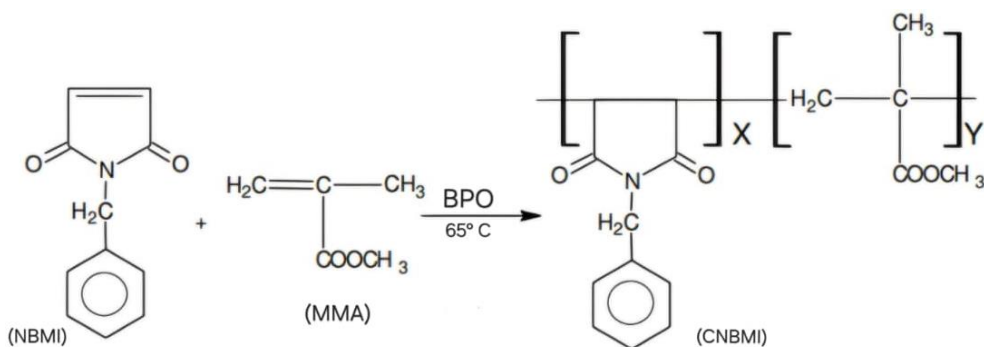


Figure 2. Copolymerization of N-Benzylmaleimide (NBMI) with Methyl Methacrylate (MMA).

N-Benzylmaleimide (NBMI) was copolymerized with methyl methacrylate (MMA) in tetrahydrofuran (THF) at 65 °C using benzoyl peroxide (BPO) as the free-radical initiator. After 24 h, the reaction mixture was transferred into an excess of methanol to precipitate the resulting copolymer. Purification was achieved through repeated dissolution in THF followed

by reprecipitation in methanol, thereby removing residual unreacted monomers and other soluble impurities. The purified copolymer was collected by filtration and dried under vacuum at 70 °C. Additional polymerization experiments were conducted using different solvent-initiator combinations. The experimental conditions and corresponding physical properties of the resulting polymers are presented in Table 1.

Table 1. At 65 °C, *N*-benzylmaleimide (NBMI) and methyl methacrylate (MMA) were subjected to free-radical polymerization and copolymerization in tetrahydrofuran (THF), using benzoyl peroxide (BPO) as the free-radical initiator.

Polymer Code	Feed Mol Ratios NBMI: MMA	Yield%	State	Color
CBMI	9:1	44.0	Solid powder	White
NBMI	9:1	39.5	Solid powder	White

2.4. Measurements

Viscosity measurements were conducted in *N*, *N*-dimethylformamide (DMF) at 30 ± 0.2 °C using an Ubbelohde viscometer. Thermogravimetric profiles were recorded in an air atmosphere using a Mettler TA-3000 thermal-analysis system. The Fourier-transform infrared (FT-IR) spectra of the synthesized monomer and polymers were obtained using a Shimadzu 8201 PC spectrometer over the range of 4000-400 cm⁻¹. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded using Bruker DPX-200 and DPX-300 spectrometers operating at 200 and 300 MHz, respectively, with DMSO-d₆ as the solvent.

3. Results and Discussions

3.1. Solubility Behaviour

The solubility behaviour of the synthesized homopolymer and copolymer was evaluated using a variety of commonly employed organic solvents, and the corresponding observations are presented in Table 2. Both the homomaleimide and copolymaleimide exhibited good-to-excellent solubility in tetrahydrofuran (THF), *N*, *N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chloroform (CHCl₃), dichloromethane, acetone, and cyclohexanone.

Table 2. Solubility behaviour of *N*-Benzylmaleimide (NBMI), Copolymer *N*-Benzylmaleimide CBMI.

S. No.	Solvent	NBMI	CBMI
1	THF	S	S
2	DMF	S	S
3	DMSO	S	S
4	Dioxane	PS	PS
5	Acetone	IS	PS
6	Chloroform	S	S
7	Ethyl acetate	S	S
8	Benzene	S	S
9	Toluene	S	S
10	CCl ₄	IS	S
11	CH ₂ Cl ₂	S	PS
12	Ethanol	IS	S
13	Methanol	S	S
14	<i>N</i> -Hexane	S	S
15	Cyclohexanone	S	S
16	Xylene	S	IS
17	1-Butanol	IS	S
18	2-Butanol	IS	IS

The comparatively broad solubility profile of these polymeric materials indicates that the synthesized structures possess favourable solvent-polymer interactions in both polar and moderately non-polar organic media. Such solubility characteristics may be advantageous for solution-based processing, purification, and characterization of the prepared polymers.

3.2. Physical Properties

The intrinsic viscosity $[\eta]$ and molecular weight of the synthesized copolymer were determined in DMF at 30 °C, and the corresponding results are presented in Table 3.

Table 3. The Physical properties of Homopolymer and Copolymer.

Polymer Code	Solvent	Temperature	$[\eta]$	Mw
CBMI	DMF	30 °C	0.060	25881
NBMI	DMF	30 °C	0.031	5675

3.3. Thermal Properties

The thermal behaviour of N-benzylmaleimide (NBMI) and its copolymer (CBMI) was investigated using thermogravimetric analysis (TGA). Measurements were conducted in an

air atmosphere at a heating rate of 10 °C min⁻¹. The thermogravimetric profile indicated that the synthesized polymaleimide underwent a single-stage degradation process above 300 °C, demonstrating its favourable thermal stability. The TGA curve of CBMI is presented in Figure 3.

Table 4. Thermodynamic properties of copolymer.

Polymer Code	Degradation Step	T _i °C	T _{max} °C	T _f °C	Residue at 500 °C
CBMI	I	190	300	550	3.70
NBMI	I	200	400	550	26.21

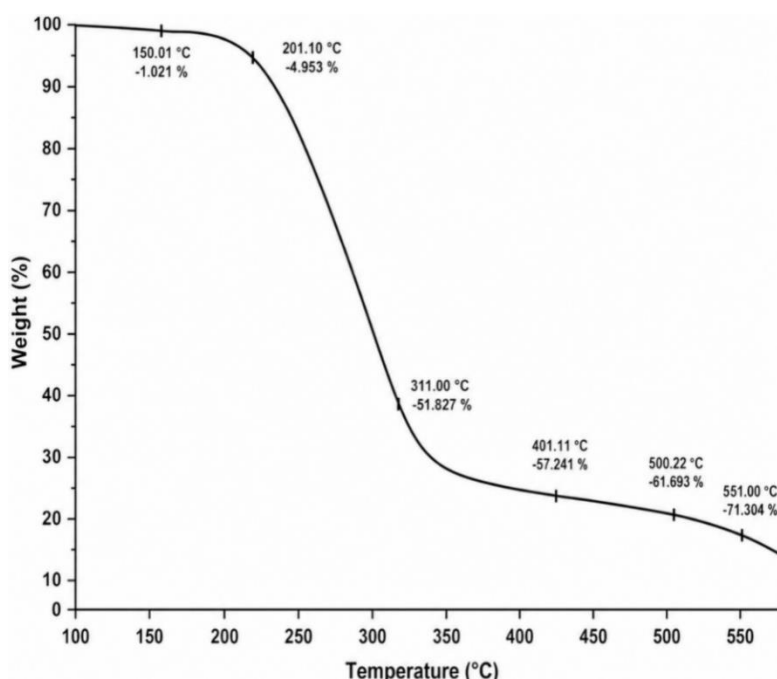


Figure 3. TGA Curve Graph for CBMI.

3.4. Spectral Characterization

The synthesized polymeric materials were characterized by FT-IR and ^1H NMR spectroscopy to establish their chemical structures and to examine the changes occurring during polymerization.

3.4.1. FT-IR and ^1H NMR Analysis of N-Benzylmaleimide (NBMI) Homopolymer

The FT-IR and ^1H NMR spectra of the N-benzylmaleimide homopolymer (NBMI), recorded in DMSO- d_6 , are presented in Figure 2. The ^1H NMR spectrum was recorded at 300 MHz.

A significant structural change upon polymerization was the disappearance of the characteristic absorption near 952 cm^{-1} associated with the olefinic functionality of the N-Benzylmaleimide (NBMI) monomer. Similarly, the ^1H NMR resonance at approximately $\delta\ 7.15\text{ ppm}$, attributed to the $\text{CH}=\text{CH}$ protons of the monomer, was no longer observed in the polymer spectrum. The disappearance of these characteristic signals indicates consumption of the maleimide double bond during polymerization and supports the occurrence of vinyl-type radical polymerization.

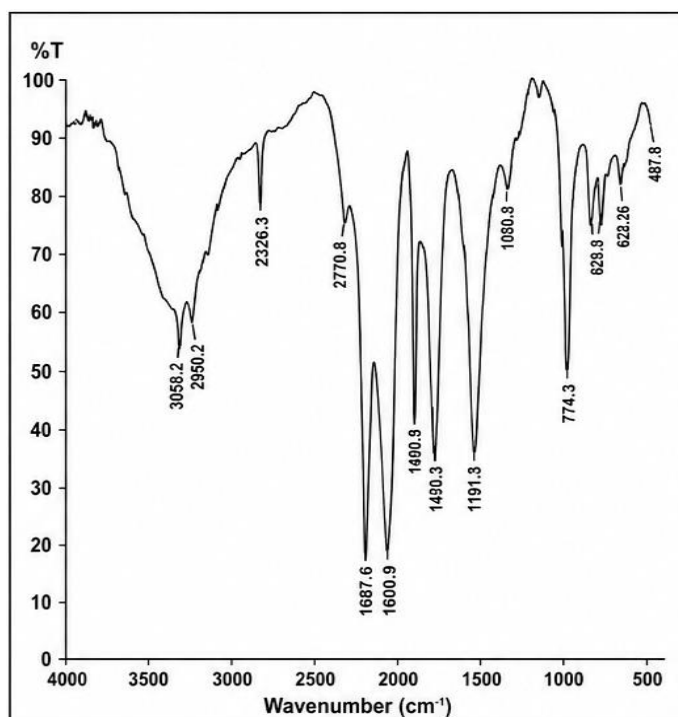
The integrity of the maleimide ring after polymerization was supported by the characteristic carbonyl absorptions observed at 1784 and 1714 cm^{-1} . These bands correspond to the

symmetric and asymmetric stretching vibrations of the carbonyl groups within the five-membered imide ring. Additional absorptions at 1466 , 1372 , 1195 , and 772 cm^{-1} were attributed to Ar-N stretching, C-N stretching, C-N-C vibrations, and characteristic imide-related vibrations, respectively. The persistence of these bands indicates that the imide functionality remained intact during the polymerization process.

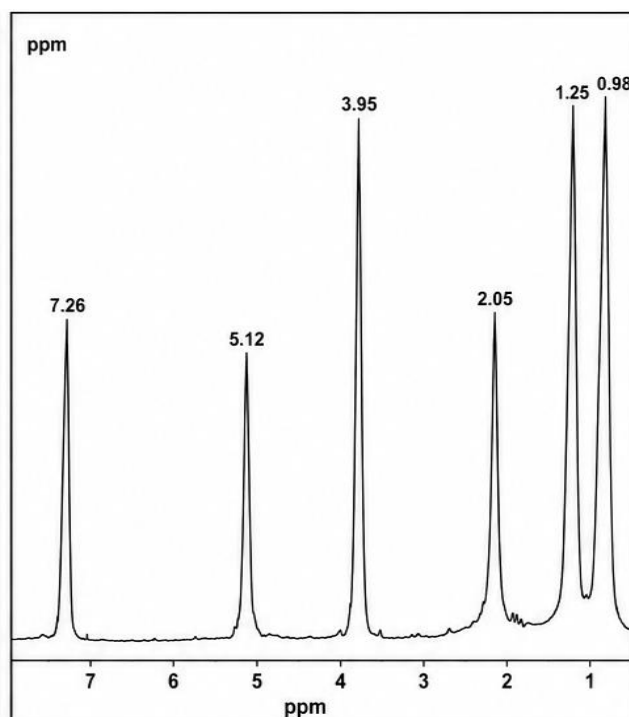
3.4.2. FT-IR and ^1H NMR Analysis of N-Benzylmaleimide (NBMI)-Methyl methacrylate (MMA) Copolymer

The structural characteristics of the N-Benzylmaleimide (NBMI)-Methyl methacrylate (MMA) copolymer were further investigated using FT-IR and ^1H NMR spectroscopy. The corresponding spectra are presented. Comparison of the monomer and copolymer spectra provides evidence for the incorporation of both N-Benzylmaleimide (NBMI) and Methyl methacrylate (MMA) structural units into the polymer chain.

In the ^1H NMR spectrum, the olefinic proton resonance of the N-Benzylmaleimide (NBMI) monomer, originally observed near $\delta\ 7.15\text{ ppm}$, was absent after polymerization. Instead, resonances associated with the saturated $-\text{CH}-\text{CH}-$ units of the polymer backbone appeared in the $\delta\ 3.4\text{--}4.1\text{ ppm}$ region. Figure 4 represents the data given respectively.



FT-IR Spectra of CBMI



^1H -NMR Spectra of CBMI

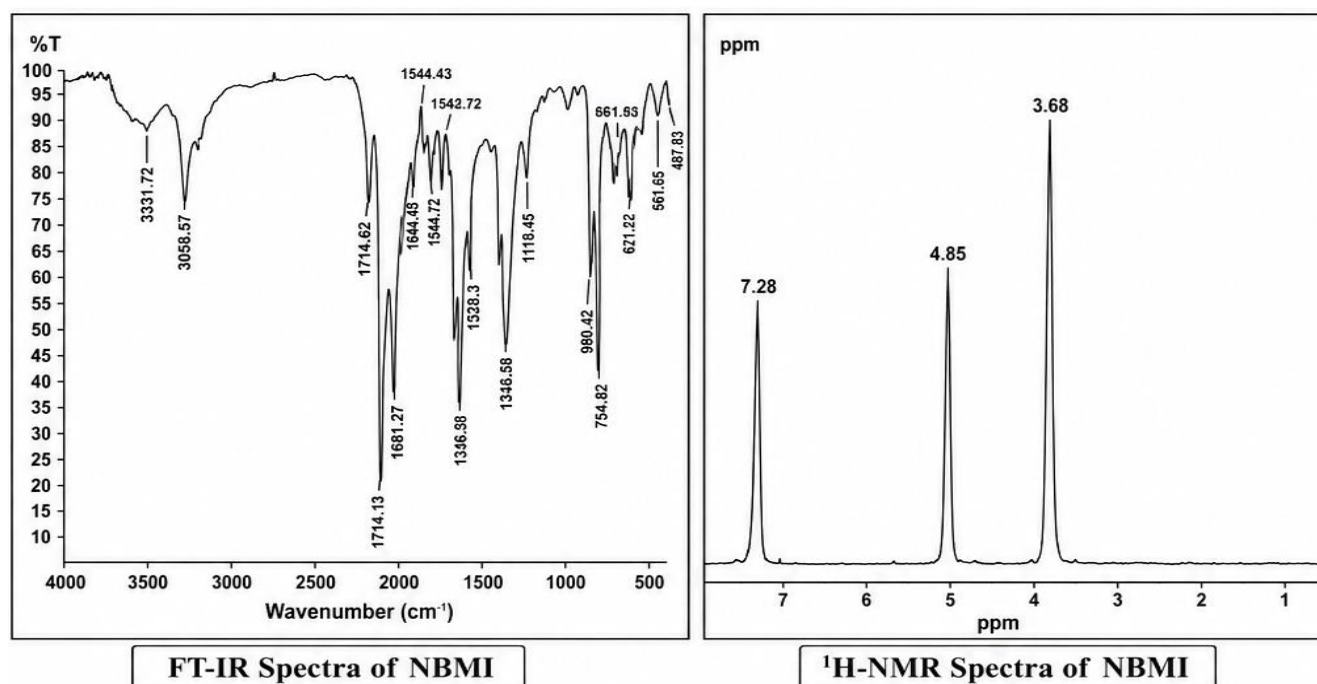


Figure 4. Represents the FTIR Spectra and ¹H-NMR of N-Benzylmaleimide (NBMI) and Copolymer (CBMI).

The aromatic protons of the benzyl/phenyl-containing structural unit produced a broad resonance in the δ 7.0–8.1 ppm region, while the characteristic benzyl methylene protons appeared at approximately δ 4.87 ppm. A group of overlapping resonances between δ 3.4 and 3.9 ppm was attributed to the methine protons of the polymer backbone together with the methoxy protons ($-\text{OCH}_3$) originating from the Methyl methacrylate (MMA) units. Signals occurring over the δ 0.84–2.4 ppm range were assigned to the methylene and methyl protons associated with the polymer backbone and Methyl methacrylate (MMA)-derived segments.

The FT-IR spectrum further supported the copolymer structure. The characteristic carbonyl absorptions at 1779 and 1714 cm^{-1} were associated with the carbonyl groups of the five-membered imide functionality and the ester carbonyl group of the MMA-derived unit. The bands at 1597 and 1512 cm^{-1} were attributed to aromatic skeletal vibrations, while the absorption at approximately 1191 cm^{-1} was associated with the C–O–C functionality of the ester group.

4. Conclusion

N-Benzylmaleimide (NBMI) was successfully copolymerized with methyl methacrylate (MMA) through free-radical polymerization at 65 °C using different solvent-initiator systems. Among the investigated combinations, tetrahydrofuran (THF) with azobisisobutyronitrile (AIBN) produced the most favourable copolymerization results. The synthesized homopolymer and copolymer exhibited good solubility in several commonly used organic solvents. Structural characterization by FT-IR and ¹H NMR spectroscopy confirmed successful

polymer formation and the retention of the imide-ring functionality. Thermogravimetric analysis further demonstrated satisfactory thermal stability, with the synthesized polymers predominantly undergoing degradation through a single-stage process. These findings indicate that NBMI-MMA copolymers possess favourable physicochemical and thermal characteristics for potential use in heat-resistant polymeric materials.

Abbreviations

NBMI	N-Benzylmaleimide
MMA	Methyl Methacrylate
THF	Tetrahydrofuran
AIBN	Azobisisobutyronitrile
BPO	Benzoyl Peroxide
FT-IR	Fourier-transform Infrared
¹ H NMR	Proton Nuclear Magnetic Resonance
GPC	Gel Permeation Chromatography
TGA	Thermogravimetric Analysis
DMSO	Dimethyl Sulfoxide
DMF	N, N-dimethylformamide
NBMA	N-Benzylmaleamic Acid

Author Contributions

Sameeksha Bansal: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Visualization, Writing – original draft

Preeti Mehta: Conceptualization, Formal Analysis, Supervision, Validation, Visualization, Writing – review & editing

Deepika Jain: Conceptualization, Methodology, Supervision, Writing – review & editing

Rajeev Mehta: Formal Analysis, Validation

Pankaj Sen: Formal Analysis, Validation

Conflicts of Interest

The authors declare no conflicts of interest.

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