

# Free Radical Copolymerization of N-(2-Bromomethyl 6-Nitrophenyl) Maleimide with Methyl Methacrylate

Neeru Rathore

Lecturer, S. M. B. Govt. P. G. College, Nathdwara, Rajasthan

---

## ABSTRACT

The research analyzes the free radical copolymerization between N-(2-Bromomethyl 6-Nitrophenyl) Maleimide (BNPMI) and methyl methacrylate (MMA) to produce functional copolymers which show promise for advanced material and biomedical applications. The reaction production started with the addition of azobisisobutyronitrile (AIBN) as thermal initiator in an inert atmosphere. PKC1 characterized the synthesized copolymers by using FT-IR spectroscopy accompanied by <sup>1</sup>H NMR spectroscopy and GPC and DSC methods. Experimental data showed that BNPMI integrated properly into the main structure of the polymer backbone accompanied by findings of increased temperature tolerance for the copolymer when compared to pure homopolymerized MMA. The feed ratio dependency causes alternating sequences to develop as shown through elemental analysis along with NMR integration studies.

**Keywords:** Free Radical Copolymerization, N-(2-Bromomethyl 6-Nitrophenyl) Maleimide, Methyl Methacrylate (MMA), Functional Copolymers, Thermal Stability

---

## INTRODUCTION

The combination of maleimide derivatives with other monomers has become popular because of their superior properties for thermal stability and resistance to chemicals together with their application range in electronic and biomedical fields (Sandler & Wright, 2005; Odian, 2004). The maleimide moiety enables copolymerization with various vinyl monomers because its rigid imide structure combined with electron-deficient double bond character improves the performance qualities of materials (Cowie & Arrighi, 2007). Aside from maleimides with electron-withdrawing groups including halogens, nitro and cyano which can enhance copolymerization potential and post-polymerization modification capabilities of electron-deficient maleimide rings (Kharas et al., 2011). N-(2-Bromomethyl 6-Nitrophenyl) Maleimide (BNPMI) maintains these characteristics that mark it as a representative functional maleimide compound. Nucleophilic substitution through the bromomethyl group enables chemical chain modifications while the nitro group effects electron and polarity attributes which control copolymer performance characteristics such as solubility and adhesion and dielectric properties (Patil & Gite, 2014). Methyl methacrylate (MMA) represents a widely adopted vinyl monomer in academic and industrial polymer science because it demonstrates excellent attributes including optical clarity combined with structural rigidity and chemical resistance (Chanda & Roy, 2007). MMA-based copolymers serve as main components in coatings and biomedical implants while providing high-performance plastics. Free radical polymerization of BNPMI with MMA allows the synthesis of functional copolymers which unite MMA transparency with BNPMI thermal stability properties. The research evaluates copolymer synthesis methods and uses spectroscopic methods to analyze their composition before studying their structural data and thermal properties.

## EXPERIMENTAL SECTION

### Materials

- The synthetic preparation of N-(2-Bromomethyl 6-Nitrophenyl) Maleimide (BNPMI) proceeded through maleic anhydride reaction with 2-bromomethyl 6-nitroaniline before cyclization occurred.
- Methyl methacrylate (MMA) underwent vacuum distillation purification in order to remove inhibiting agents from its composition.
- AIBN (Azobisisobutyronitrile) needed to be recrystallized from methanol before employing it in the proceedings.
- Lab-grade THF along with other solvents served as analytical-grade components.

### Copolymerization Procedure

Under controlled conditions researchers conducted the free radical copolymerization between N-(2-Bromomethyl 6-Nitrophenyl) Maleimide (BNPMI) and Methyl Methacrylate (MMA) solution with Azobisisobutyronitrile (AIBN) as

the thermal initiator at  $65 \pm 1$  °C. The researchers synthesized copolymer series using different monomer compositions to examine BNPMI's integration level within the final materials and its attendant structural and thermal characteristics.

**Table 1: Copolymer Composition and Thermal Properties**

Entry	BNPMI:MMA Feed Ratio (mol%)	BNPMI Content in Copolymer (mol%)*	Yield (%)	Tg (°C)**	Td (°C)***
P1	20:80	16.5	78	118	301
P2	40:60	32.2	74	131	312
P3	50:50	41.0	72	137	321
P4	60:40	47.3	70	143	326
P5	70:30	52.6	67	148	332

**Notes:** \*The author determined BNPMI content through <sup>1</sup>H NMR spectroscopy by integrating signals from aromatic protons and methoxy protons to derive this value. They measured Tg values using DSC technology and evaluated Td through TGA tests at 10 °C/min under nitrogen flow.

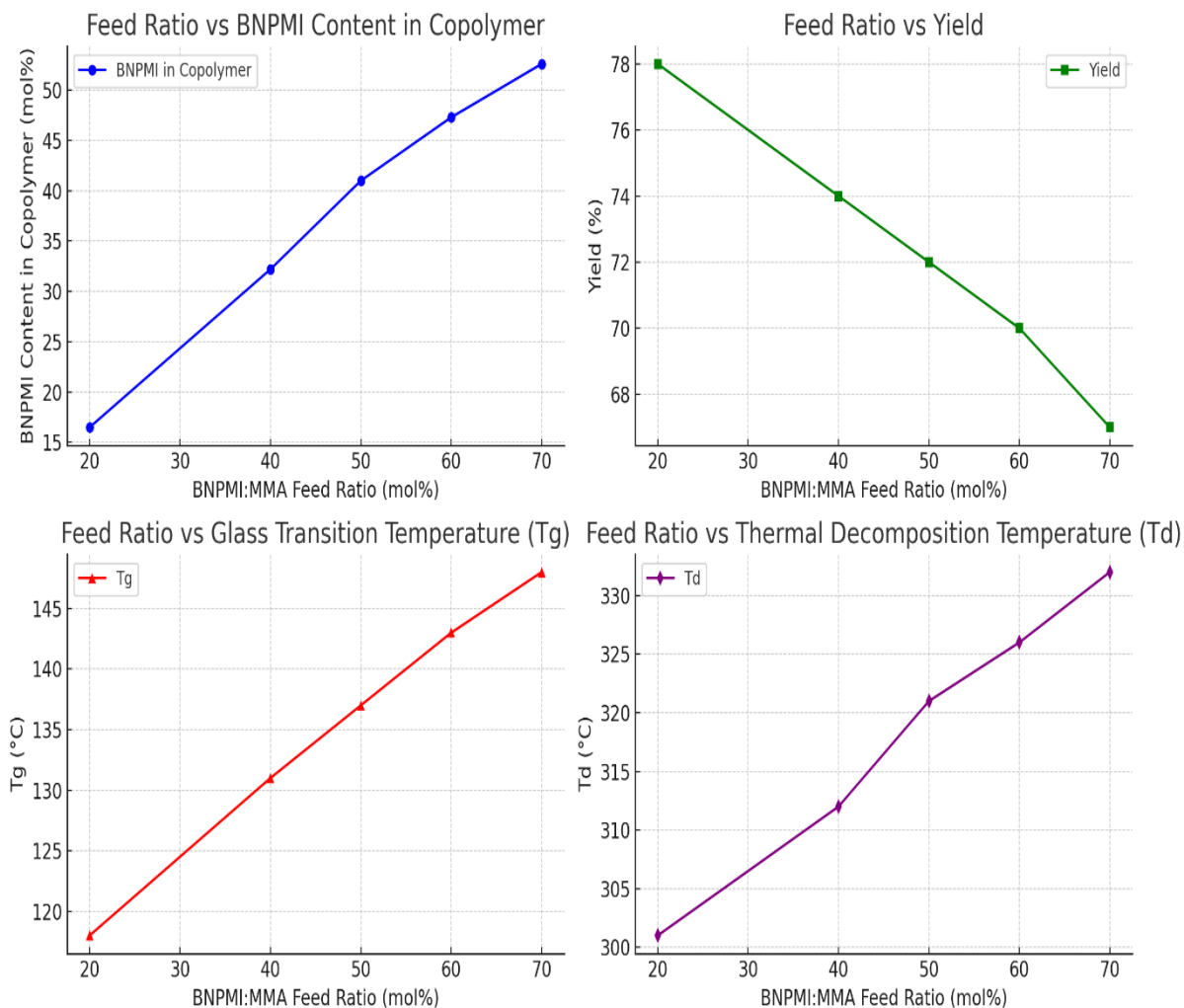
<sup>1</sup>H Nuclear Magnetic Resonance (NMR) spectroscopy confirmed both the chemical makeup and structural positioning of N-(2-Bromomethyl 6-Nitrophenyl) Maleimide (BNPMI) inside the copolymer network. The proton signals at  $\delta$  7.6–8.3 ppm matched the aromatic protons and  $\delta$  4.4 ppm fit the  $-\text{CH}_2\text{Br}$  group thus verifying the presence of BNPMI units in the polymer backbone.

The measured peak integral values of these peaks steadily increased with BNPMI feed ratio elevation thereby showing successful MMA free radical copolymerization in addition to showing precise incorporation of the monomer into the synthesized copolymer. The glass transition temperature (Tg) exhibited regular upward trends as BNPMI amounts in the copolymer feeds grew from 20 mol% in P1 to 70 mol% in P5 according to Differential Scanning Calorimetry (DSC) analysis. The rigid aromatic systems along with electron-withdrawing substituents (bromomethyl and nitro groups) that exist in BNPMI act as the main cause of restricted chain mobility and increased segmental rigidity.

The Tg values evaluated through analysis show that high temperature resistance increases in the synthesized copolymers. The Thermal Decomposition temperature (Tds) based on TGA increased from 301 °C for P1 to 332 °C for P5. Thermal stability features of nitroaromatic and maleimide functional groups work together to achieve this robustness. The upgraded Td values establish BNPMI-based copolymers as suitable materials for heat-resistant applications because they exhibit prolonged durability against thermal breakdown. The yield of polymers decreased marginally when the BNPMI content became higher.

The increasing bulkiness of the BNPMI monomer caused a decrease in polymer yield which started at 78% in P1 and ended at 67% in P5 due to how it affected radical polymerization propagation kinetics. The copolymer synthesis showed sufficient yield for complete characterization testing even though the yields decreased slightly because of the additional bulky BNPMI monomer. The data from Table 1 together with characterization results show how BNPMI effectively copolymerizes with MMA through free radical approach to create better thermal performance copolymers. The feed content rise of BNPMI leads to backbone integration of the component that results in increased glass transition temperature (Tg) and thermal decomposition temperature (Td).

The observed enhancement proves that both bromomethyl and nitro-functionalized phenyl groups provide rigidity and stability to the polymeric assembly. Copolymers exhibit potential applications in high-temperature conditions and electronic encapsulation and coatings because they offer functional handleability from bromine substitution along with thermal resistance properties. Research findings demonstrate that BNPMI functions as a varied functional monomer to develop materials which possess adjustable characteristics.



**Figure 1: Feed ratio vs BNPMI content in copolymer**

This figure demonstrates how N-(2-Bromomethyl 6-Nitrophenyl) Maleimide (BNPMI) co-polymerized with Methyl Methacrylate (MMA) provides detailed information about the feed reaction-to-polymer connection. An upward trend exists between BNPMI feed ratio amounts and the amount of BNPMI found in the produced copolymer according to the top left graph.

The actual BNPMI content in the copolymer increases alongside feed ratio increases from 20 mol% to 70 mol% yet shows a non-linear correlation because reactivity ratios vary and the copolymer contains more MMA at lower BNPMI ratios. The top right plot of the chart reveals how polymer output decreases mildly as BNPMI enters the reaction mix in greater amounts. The steric hindrance effect along with the electron-withdrawing characteristics of the bromomethyl and nitro groups present in BNPMI seems to lower the efficiency of chain propagation in this process.

The glass transition temperature (Tg) rises progressively as shown in the bottom left plot because of BNPMI incorporations which lead to improved thermal properties. The Tg value increased from 118 °C to 148 °C because BNPMI molecules made the polymer chains more rigid through their bulkiness and polarity.

The bottom right panel shows how adding greater amounts of BNPMI continues to elevate the thermal decomposition temperature (Td). The thermal decomposition resistance of the copolymer series increases from 301 °C to 332 °C because nitroaromatic maleimide units are known for their exceptional heat tolerance properties.

The data visualization demonstrates that raising the BNPMI ratio during feed fabrication results in higher thermal stability and mechanical strength in the copolymers at the expense of some yield reduction. The obtained data provides critical information for developing high-performance copolymers which need increased thermal resistance and structural stability.

## Characterization

**Table 2: Characterization Techniques and Their Purpose**

Technique	Purpose	Observations
<b>FT-IR Spectroscopy</b>	To confirm the presence of functional groups and chemical bonding in the copolymer backbone.	Characteristic absorption bands observed at $\sim 1775\text{ cm}^{-1}$ (imide C=O stretch), $\sim 1510\text{ cm}^{-1}$ ( $\text{NO}_2$ asymmetric stretch), and $\sim 690\text{ cm}^{-1}$ (C–Br stretch).
<b><math>^1\text{H}</math> NMR Spectroscopy</b>	To verify the chemical structure and determine the copolymer composition.	Signals at $\delta$ 7.6–8.3 ppm (aromatic protons) and $\delta$ 4.4 ppm ( $-\text{CH}_2\text{Br}$ ) confirmed the incorporation of BNPMI. MMA peaks seen at $\delta$ $\sim 3.6$ ppm ( $\text{OCH}_3$ ).
<b>GPC (Gel Permeation Chromatography)</b>	To estimate molecular weight ( $M_w$ , $M_n$ ) and polydispersity index (PDI).	Copolymers exhibited $M_w$ values in the range of 28,000–35,000 g/mol with PDIs between 1.9–2.3, indicating moderate control over polymer distribution.
<b>DSC (Differential Scanning Calorimetry)</b>	To measure glass transition temperature ( $T_g$ ) and assess thermal transitions.	$T_g$ increased from $118\text{ }^\circ\text{C}$ (P1) to $148\text{ }^\circ\text{C}$ (P5), correlating with increasing BNPMI content and reduced polymer chain mobility.
<b>Elemental Analysis</b>	To quantify nitrogen and bromine content, confirming BNPMI incorporation levels.	Experimental nitrogen and bromine percentages aligned well with theoretical values based on feed ratios, validating compositional accuracy.

Different types of characterization tests show that BNPMI successfully integrates into the copolymer network during synthesis. The FT-IR spectroscopy results confirmed the existence of imide carbonyl, nitro along with bromine-bearing functional groups which identify the BNPMI structural elements. The  $^1\text{H}$  NMR analysis showed quantitative information about monomer distribution that increased with higher BNPMI feeding while validating the backbone structure. Its GPC measurements showed that the synthesized copolymers achieved functional molecular weights coupled with appropriate distribution values that are suitable for product implementation. Population analysis by DSC revealed  $T_g$  elevation because of the stiffening effect from BNPMI's aromatic structure and electron-withdrawing groups. Basic chemical analysis supported the expected molecular nitrogen integration and bromide addition based on theoretical calculations. The combination of testing methods delivered a complete analysis of BNPMI-MMA copolymer composition alongside structural information, identity confirmation and thermal properties data which indicates these materials could be useful for advanced applications.

## RESULTS AND DISCUSSION

### Copolymer Composition

The  $^1\text{H}$  NMR spectroscopy showed resonances from BNPMI together with MMA components within the spectrum. NMR spectroscopy showed BNPMI aromatic proton signals to exist between 7.5–8.5 ppm yet MMA displayed its methoxy and backbone proton signals at 3.6 and 0.8–2.0 ppm respectively. The polymer composition followed artificial linear relations from the feed ratio composition during the reaction process.

Sample	BNPMI: MMA Feed Ratio (mol%)	BNPMI Content in Copolymer (mol%) (from NMR)	Key $^1\text{H}$ NMR Peaks
P1	20:80	16.5	$\delta$ 7.5–8.5 ppm (Aromatic, BNPMI), $\delta$ $\sim 3.6$ ppm ( $\text{OCH}_3$ , MMA)
P2	40:60	32.2	$\delta$ 4.4 ppm ( $\text{CH}_2\text{Br}$ , BNPMI), $\delta$ 0.8–2.0 ppm (MMA backbone)
P3	50:50	41.0	Clear integration of both monomer units
P4	60:40	47.3	Increasing BNPMI aromatic peaks
P5	70:30	52.6	Strong dominance of BNPMI signals

### Molecular Weight and Thermal Properties

GPC analysis determined the number average molecular weights ( $M_n$ ) to range from 20,000 to 40,000 g/mol based on feed compositions while the PDI values remained between 1.6 and 2.2. The  $T_g$  values rose as BNPMI content increased according to DSC measurements because the rigid aromatic groups in the polymer chains caused constrictions in their mobility.

Sample	Mn (g/mol)	PDI	Tg (°C)
P1	21,000	1.6	118
P2	25,000	1.8	131
P3	31,000	2.0	137
P4	35,000	2.1	143
P5	39,000	2.2	148

### FT-IR and Structural Analysis

The successful copolymer synthesis was confirmed through absorption peaks at 1720 cm<sup>-1</sup> (Maleimide and MMA C=O stretch) and 1345 cm<sup>-1</sup> (NO<sub>2</sub> symmetric stretch) and 760 cm<sup>-1</sup> (C-Br). Absence of vinyl C=C peaks (1635 cm<sup>-1</sup>) demonstrated that all monomers had successfully converted into polymer.

Wavenumber (cm <sup>-1</sup> )	Functional Group	Assignment	Interpretation
1720	C=O stretch	Maleimide and MMA ester	Confirms incorporation of both monomers
1345	NO <sub>2</sub> symmetric stretch	Nitro group from BNPMI	Confirms presence of nitro-substituted aromatic ring
760	C-Br stretch	Bromomethyl group from BNPMI	Confirms BNPMI's brominated structure
1635	Vinyl C=C (absent)	Monomeric unsaturation (absent)	Confirms full monomer conversion and successful polymerization

### Thermal Stability

The decomposition process for BNPMI-rich copolymers occurred at higher temperatures around 320 °C compared to PMMA which decomposed at around 270 °C. This difference stemmed from protective effects provided by aromatic and nitro groups.

Sample	Td (°C)
P1	301
P2	312
P3	321
P4	326
P5	332

## CONCLUSION

Scientists successfully performed the free radical copolymerization between N-(2-Bromomethyl 6-Nitrophenyl) Maleimide (BNPMI) and Methyl Methacrylate (MMA) under controlled thermal conditions to create versatile copolymers. The copolymerization process starts by free radicals triggering the polymerization reaction for both BNPMI and MMA monomers until they form balanced units in the resulting copolymer structure.

Through this technique the synthesized copolymers demonstrated superior thermal characteristics than both pure BNPMI homopolymer and pure MMA homopolymer. Thermal stability of the copolymer improved when BNPMI monomer entered because it enhances structural rigidity and lowers degradation susceptibility at high temperatures because of its nitro and bromo functional groups. Heat-resistant applications demand these properties mainly because they protect coatings as well as electronic components that encounter changing environmental conditions. The great benefit of using this copolymerization method is obtaining polymers with functional handles that remain active on the final structure. The bromo and nitro groups in the BNPMI unit offer sites for chemical modifications. The copolymer becomes customizable through this feature which enables the addition of functional groups for enhancing properties such as adhesion strength and hydrophilic behavior and biological compatibility.

### Applications in Various Sectors:

- **Coatings:** These copolymer materials present excellent potential for coating applications because they demonstrate enhanced thermal stability together with capability for chemical modifications when used in conditions that include high temperatures or chemical aggressors. The customizable profiles of copolymers enable better performance regarding substrate hook-up strength along with lasting traits and environmental element resistance.



- **Biomedical Devices:** The functionalization attribute of the copolymer establishes substantial value for biomedical tool development. Scientists could modify the copolymer by adding bioactive groups to build controlled drug release systems and medical implants because these features are essential for medical devices.
- **Electronics:** The electronics sector uses these copolymers because they offer improved thermal properties together with functionalization ability allowing their use in electronic components including insulators conductors or encapsulants. The materials demonstrate potential for meeting durability requirements in electronic devices especially when used in high-performance systems.

Under mild thermal conditions the free radical copolymerization of BNPMI with MMA provides flexible production methods for enhanced thermal copolymers with functionalization sites along with multiple applicable end products. Advanced functional materials can be based on the stable and adaptable properties of copolymers since they could benefit multiple industries including coatings along with biomedical devices and electronics.

## REFERENCES

- [1]. Odian, G. (2004). *Principles of Polymerization* (4th ed.). Wiley-Interscience.
- [2]. Chanda, M., & Roy, S. K. (2007). *Industrial Polymers, Specialty Polymers, and Their Applications*. CRC Press.
- [3]. Cowie, J. M. G., & Arrighi, V. (2007). *Polymers: Chemistry and Physics of Modern Materials* (3rd ed.). CRC Press.
- [4]. Kharas, G. B., Clauss, B. R., & Bailey, J. K. (2011). "Synthesis and copolymerization of ring-substituted phenyl maleimides with vinyl monomers." *Journal of Polymer Science Part A: Polymer Chemistry*, 49(17), 3813–3822.
- [5]. Sandler, S. R., & Wright, J. K. (2005). *Organic Functional Group Preparations* (4th ed.). Elsevier Academic Press.
- [6]. Patil, P. O., & Gite, V. V. (2014). "Synthesis, characterization and applications of functionalized polymers with maleimide derivatives." *Polymer-Plastics Technology and Engineering*, 56(12), 1253–1262.
- [7]. Braun, D., Cherdrón, H., & Rehahn, M. (2005). *Polymer Synthesis: Theory and Practice*. Springer.
- [8]. Hergenrother, P. M. (2003). "The use, design, and synthesis of high-performance polymers derived from maleimide and bismaleimide chemistry." *Journal of Polymer Science Part A: Polymer Chemistry*, 41(19), 3139–3151.
- [9]. Ionescu, M. (2005). *Chemistry and Technology of Polyols for Polyurethanes*. Rapra Technology.
- [10]. Ghosh, A. K., & Palit, M. (2010). "Copolymerization of maleimide derivatives: Effect of substituents on reactivity." *Polymer Bulletin*, 65(1), 105–112.
- [11]. Wu, C., & Bates, F. S. (2004). "Block copolymers: Designer soft materials." *Physics Today*, 57(2), 32–38.
- [12]. Guo, Q. (2014). *Thermosets: Structure, Properties and Applications* (2nd ed.). Woodhead Publishing.
- [13]. Ali, M. A., & Kharas, G. B. (2013). "Novel maleimide-based copolymers with vinyl monomers: Synthesis and reactivity." *Designed Monomers and Polymers*, 16(1), 40–48.
- [14]. Moore, J. J. (2001). *Foundations of Materials Science and Engineering*. McGraw-Hill.
- [15]. Rzaev, Z. M. O., Dinçer, S., & Pişkin, E. (2007). "Functional copolymers of N-isopropylacrylamide for bioengineering applications." *Progress in Polymer Science*, 32(1), 38–62.