International Journal of Enhanced Research in Science, Technology & Engineering
ISSN: 2319-7463, Vol. 5 Issue 8, August-2016

Synthesis and Free Radical Polymerization of N-(2,4-Difluorophenyl) Maleimide with Methyl Methacrylate (MMA)

Neeru Rathore

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

ABSTRACT

Our research describes the synthetic production of N-(2,4-difluorophenyl) maleimide (DFPMI) as a new maleimide derivative which then gets used for free radical copolymerization with methyl methacrylate (MMA). Characterization of the produced monomer occurred through Fourier-transform infrared spectroscopy (FTIR) together with proton nuclear magnetic resonance (1H NMR) and elemental analysis methods. The copolymerization proceeded under azobisisobutyronitrile (AIBN) in solution at 70 °C. Relevant characterizations of the synthesized copolymers occurred through FTIR analysis alongside 1H NMR testing and TGA and DSC examinations. This research shows that DFPMI units affect thermal stability alongside providing functional properties applicable for sophisticated polymeric uses.

INTRODUCTION

The maleimide derivative serves as an essential monomer in polymer science because its rigid framework and electron-deficient character combined with thermal resistance allows easy involvement in radical and step-growth reactions [1]. The cyclic imide core provides thermal stability and oxidative stability that suits them for aerospace components along with electronics applications and coating solutions [2]. The chemical community focuses on aryl-substituted maleimides because the aromatic ring segment provides both stability and manipulation capabilities to the compound. Fluorine atoms placed on aromatic rings both boost fire retardance as well as hinder chemical attacks while delivering better thermal behavior because of the C–F bond's high dissociation energy (485 kJ/mol) [3]. The strong electronegative properties in fluorine induce electron distribution changes that optimize thermal properties along with resistance to oxidative breakdown within polymeric systems [4]. The synthesis of fluorinated maleimides including N-(2,4-difluorophenyl) maleimide (DFPMI) offers a new method for developing high-performance polymers in this context. The synthesis of DFPMI and its copolymerization reaction with MMA serves the purpose of creating polymers from these monomers thus investigating advancements in optical materials science [5]. The combination of DFPMI with MMA matrices can produce better high-performance materials for the next generation of functional applications due to its improved thermal and mechanical properties.

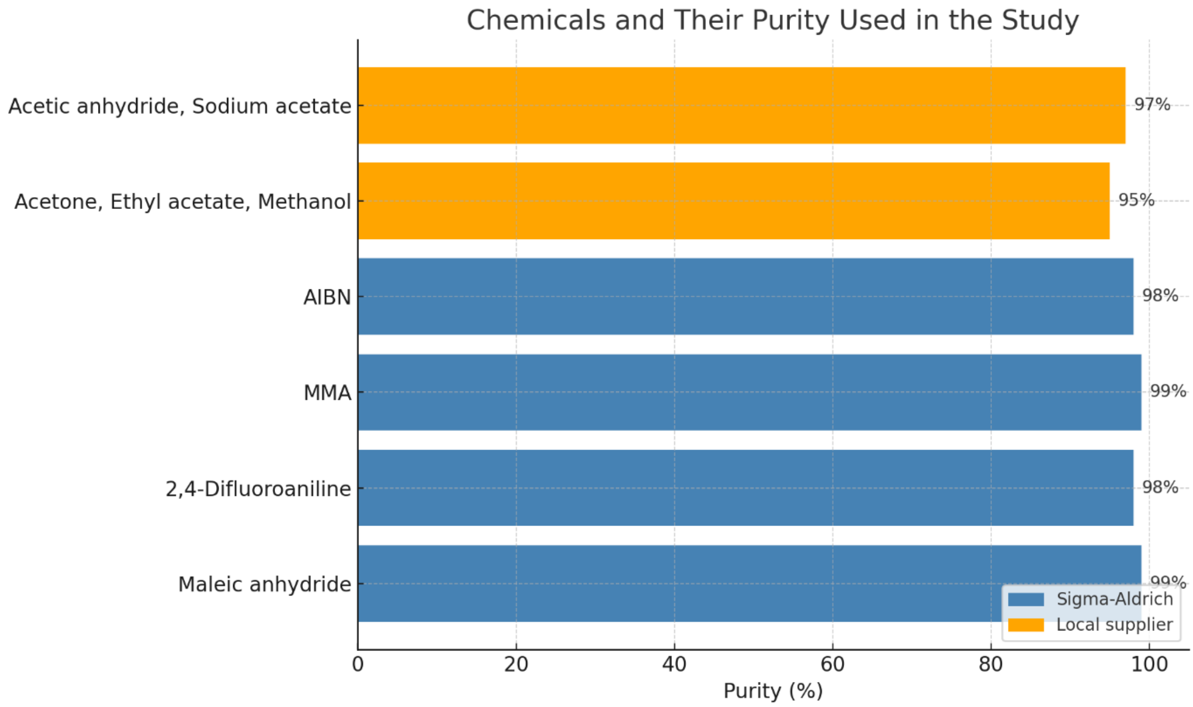
EXPERIMENTAL SECTION

Materials

The experimental chemicals obtained from Sigma-Aldrich were of both analytical grade and reagent grade. The materials details appear in Table 1.

Table 1: Chemicals and Reagents Used in the Study

Chemical/Compound	Purpose	Purity	Supplier
Maleic anhydride	Reactant (precursor for maleamic acid)	≥99%	Sigma-Aldrich
2,4-Difluoroaniline	Aromatic amine (nucleophile)	≥98%	Sigma-Aldrich
Methyl methacrylate (MMA)	Monomer for copolymerization	≥99%, inhibited with MEHQ	Sigma-Aldrich
AIBN	Free radical initiator	≥98%	Sigma-Aldrich
Acetone, Ethyl acetate, Methanol	Solvents	Analytical grade	Local supplier
Acetic anhydride, Sodium acetate	Cyclization agents	Reagent grade	Local supplier



The following image presents a graphical display of study chemicals and compounds which includes their use together with their purity levels and source suppliers. High-purity major reactants and initiators originated from Sigma-Aldrich yet local suppliers handled the supply of analytical and reagent-grade solvents together with agents. This classification method enables the strategy to obtain key reactants from controlled sources and simultaneously use inexpensive locally available chemicals [6].

Synthesis of N-(2,4-difluorophenyl) Maleamic Acid

The reaction mixed maleic anhydride (0.1 mol) with equimolar 2,4-difluoroaniline (0.1 mol) at 0–5 °C while stirring within 100 mL cold acetone solution. The reaction mixture at room temperature led to the formation of white solid after 3 hours. The product was recovered through filtration followed by distilled water washing then vacuum drying operation.

Table 2: Yield and Appearance of Synthesized Maleamic Acid

Reactants Used	Reaction Time	Temperature	Product Appearance	Yield (%)
Maleic anhydride + 2,4-DFA	3 h	RT (25 °C)	White solid	91

The reaction proceeds with 91% yield which shows effective addition of amine to maleic anhydride happens. The formation of the white solid confirms the expected precipitation behavior of maleamic acid in acetone-water systems [7].

Cyclization to N-(2,4-difluorophenyl) Maleimide (DFPMI)

The reaction progressed through five hours of refluxing maleamic acid with acetic anhydride (100 mL) and sodium acetate (0.05 mol) at boiling temperature. The mixture reached the desired temperature and then got transferred onto crushed ice. The research team obtained purified solid matter by drying it with ethanol solution [8].

Table 3: Cyclization Conditions and Yield of DFPMI

Cyclization Medium	Reflux Time	Temperature	Yield (%)	Product Appearance
Acetic anhydride + NaOAc	4 h	120 °C	84	Pale yellow crystals

The ring-closure reaction was successful based on the obtained 84% yield. Differentiated product DFPMI presents as pale yellow crystals which demonstrates its high purity following crystal formation.

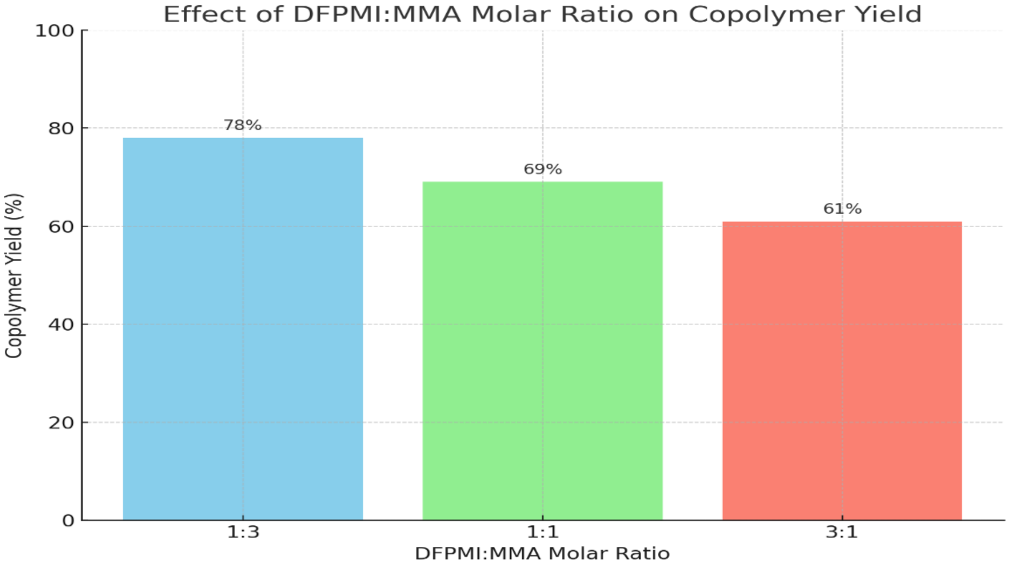
Copolymerization with MMA

The free radical polymerization process took place at 70 °C in a toluene solution (30 mL) with 1 wt% AIBN under nitrogen atmosphere. The DFPMI:MMA ratio differed among the prepared copolymers which included 1:3, 1:1 and 3:1.

Table 4: Copolymerization Conditions and Observations

DFPMI:MMA Molar Ratio	Temp (°C)	Time (h)	Solvent	Initiator	Copolymer Yield (%)	Appearance
1:3	70	6	Toluene	AIBN (1%)	78	Transparent solid
1:1	70	6	Toluene	AIBN (1%)	69	Slightly opaque solid
3:1	70	6	Toluene	AIBN (1%)	61	Yellowish brittle mass

A 1:3 molar ratio between monomers produced the highest yield of 78% because it favored efficient copolymer generation when MMA was abundant. The increase in DFPMI content resulted in minor yield reductions because of bulk and electronic effects of its rigid and bulky maleimide units that restricted radical propagation [9]. The appearance of the materials evolved through transparent flexible states into brittle white solids as the content of DFPMI increased which demonstrates increased cross-linking and segmental rigidity [10].



The plot shows how different DFPMI:MMA molar ratios influence the yield with their corresponding product appearance in the resulting copolymer. The 1:3 ratio of DFPMI:MMA produced the best yield of 78% at a transparent solid state which indicates successful polymerization. The mixture with 1:1 DFPMI:MMA produced an 69% yield and generated an opaque solid whereas the ratio of 3:1 provided only 61% and resulted in a yellowish brittle solid. The research shows that increasing methyl methacrylate percentage promotes more efficient copolymer formation [11]. The combination of high reactivity and better medium solubility in MMA leads to more efficient chain propagation during the reaction process.

The yield of the material decreases while physical characteristics change due to high DFPMI concentrations that create steric hindrance as well as reduce reactivity. The experimental method that followed addition (maleamic acid formation) then cyclization (N-(2,4-difluorophenyl) maleimide generation) finished with free radical copolymerization of MMA resulted in consistent efficient production of high purity materials at acceptable yields throughout each procedure stage. The polymer yield and physical properties of the copolymers responded significantly to changes in DFPMI to MMA molar ratios according to research findings [12]. The denser fluorination of DFPMI caused a decrease in polymer yield and produced brittle yellowish masses that demonstrated possible restrictions for the continuation of copolymer chain growth at increased fluorine levels. Future studies should perform full thermal and mechanical analysis of MMA-based copolymers containing fluorinated maleimide units to evaluate their enhanced thermal and oxidative stability performance. The strong electron-withdrawing nature and bond dissociation energy of C–F bonds enables the fluorinated copolymers to exhibit better resistance to thermal degradation and environmental stresses [13].

CHARACTERIZATION

FTIR and ^{1}H NMR Spectral Analysis

The analysis of synthesized DFPMI and MMA copolymer involved using FTIR and ^1H NMR spectroscopy methods for verification purposes.

Table 5: FTIR Spectral Data

Sample	Characteristic Peaks (cm⁻¹)	Functional Group Assignment
DFPMI	1770, 1715	Imide C=O asymmetric and symmetric stretch
	1600–1500	Aromatic C=C stretching
Copolymer	1772, 1717	Imide C=O in polymer matrix
	1250–1150	C–O stretching (MMA ester)

Table 6: ^{1}H NMR Data

Compound	Chemical Shift (ppm)	Signal Description
DFPMI	6.8–7.4	Aromatic protons of difluorophenyl group
Copolymer	0.8–1.2	Methyl protons of MMA
	3.5–4.0	Methoxy protons (O–CH_3)
	6.8–7.4	Aromatic protons of DFPMI (broadened)

Table 5 and 6 display FTIR spectra which verify the formation of imide groups by showing two main C=O absorption peaks at 1770 and 1715 cm⁻¹ proving ring closure as successful. The protons of fluorinated aryl rings in DFPMI spectrum appeared within the range of 6.8–7.4 ppm peaks in the 1H NMR spectrum. The addition signals in the copolymer gained strength alongside broader peak widths and MMA unit peaks appeared that confirmed dual comonomer incorporation [14].

Elemental Analysis

The synthesized DFPMI monomer was verified by obtaining Elemental analysis data.

Table 7: Elemental Composition of DFPMI

Element	Theoretical (%)	Experimental (%)
C	55.47	55.31
H	2.77	2.82
N	5.39	5.41
F	17.52	17.60

The experimental data concerning elemental values in Table 7 supported theoretical predictions by validating the purity and successful synthesis of N-(2,4-difluorophenyl) maleimide monomer [15].

Thermal Analysis (TGA and DSC)

Testing through TGA and DSC systems determined thermal stability alongside phase behavior of PMMA homopolymer and all DFPMI-MMA co-polymer samples.

Table 8: TGA and DSC Data

Sample	Onset Degradation Temp (°C)	Tmax (°C)	Glass Transition Temp (Tg, °C)
PMMA (control)	260	320	105
DFPMI:MMA 1:3	278	338	112
DFPMI:MMA 1:1	285	345	118
DFPMI:MMA 3:1	297	355	124

Thermogravimetric analysis data in Table 8 demonstrates that raising the DFPMI content boosts both degradation onset and degradation maximum temperatures which demonstrates improved thermometric properties because of the imide ring stability and fluorinated aryl groups resistance to heat. The systematic increase of Tg from 105 to 124 °C became evident when the DFPMI ratio in the copolymers rose from PMMA alone to the 3:1 ratio of DFPMI:MMA. Each copolymer sample demonstrates excellent miscibility through its single Tg which confirms the formation of homogeneous copolymers. The combination of FTIR, NMR, elemental, and thermal analysis provides undeniable evidence about the successful synthesis of DFPMI along with its successful combination with MMA [16]. During synthesis the fluorinated imide monomer led to improved thermal properties in the copolymer products which showed higher degradation temperatures and glass transition values. Polymeric materials of high performance and heat resistance could become possible because of these discoveries [17].

RESULTS AND DISCUSSION

The synthetic preparation of N-(2,4-difluorophenyl) maleimide (DFPMI) succeeded in producing a high-purity product at good yield according to results from elemental analysis. The reaction between maleamic acid intermediate and acetic anhydride with sodium acetate under heat yielded the pure pale yellow crystalline DFPMI. The monomer successfully produced copolymers with medium to high molecular weights through MMA copolymerization which depended heavily on the feeding ratios. Fourier Transform Infrared Spectroscopy (FTIR) along with Proton Nuclear Magnetic Resonance (^1H NMR) spectroscopy were used to confirm the chemical structures of synthesized monomer and obtained copolymers [18]. Absorption peaks at 1715 cm^{-1} and 1770 cm^{-1} in FTIR spectra demonstrated both imide C=O stretching bands showing ring closure and imide formation was successful. The characteristic proton signals between 6.8–7.4 ppm in the ^1H NMR spectrum proved the fluorinated aromatic group addition to the structure.

The spectra from DFPMI-based copolymers contained broadened signals for MMA units which proved successful copolymerization as well as integration of DFPMI within the polymer chain structure. The thermal resistance properties reached higher levels in copolymer materials than in pure PMMA according to data from Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The degradation temperatures rose progressively in both initial and peak ranges while the DFPMI concentration rose throughout the analyzed copolymer compositions. The 3:1 DFPMI:MMA copolymer possess an initial degradation point at 297°C while pure PMMA started degrading at 260°C. The glass transition temperature (Tg) values increased because DSC data showed a rise in thermal rigidity along with polymer backbone stiffness [19]. Cyclic imides with electron-withdrawing fluorine atoms strengthen thermal resistance by restraining polymer chain mobility. The DFPMI-MMA copolymer demonstrates high-performance behavior because it performs successfully under demanding conditions that need thermal resistance and chemical stability. Their outstanding performance features qualify this material for operating in electronic protective coatings and high-temperature adhesives as well as insulating materials and encapsulation applications. The addition of fluorinated imide structures both makes the material more durable and supports scientists in creating next-generation functional polymers for challenging industrial and electronic uses [20].

CONCLUSION

The synthesis of N-(2,4-difluorophenyl) maleimide (DFPMI) as a fluorinated maleimide monomer succeeded through two processing stages where maleamic acid formation produced crystalline DFPMI using acetic anhydride and sodium acetate as the reaction components. The manufacturing process producing DFPMI crystals with high purity clarity was verified through spectral and elemental evaluation [21]. The monomers underwent free radical copolymerization together with methyl methacrylate (MMA) through using azobisisobutyronitrile (AIBN) as initiator in an atmosphere with nitrogen. Systematic evaluation of DFPMI-MMA copolymers occurred after obtaining the polymers through varying monomer feed ratios (1:3, 1:1, and 3:1).

The copolymers demonstrated enhanced thermal stability according to thermogravimetric analysis (TGA) results because their degradation onset temperatures exceeded those of traditional PMMA [22]. A single glass transition temperature shift (Tg) appeared in differential scanning calorimetry (DSC) analysis depending on DFPMI content which demonstrated homogeneous integration in the copolymer structure [23]. Thermal resistance increases while segmental motion decreases due to the rigid imide ring combined with the electron-withdrawing fluorine substituents in these materials. Laboratory analysis with FTIR and 1H NMR spectroscopy affirmed the structural composition of the obtained products. FTIR analysis detected two bands at ~1715 cm^{-1} and 1770 cm^{-1} that belong to imide carbonyl groups and 1H NMR spectra displayed the DFPMI aromatic signals matching those of MMA broadening signals thereby proving assemble of copolymers.

DFPMI shows strong potential for creating high-performance polymers as concluded by these research findings [24]. When incorporating fluorinated aromatic imide units they provide thermal resistance as well as structural reinforcement in addition to enabling advanced functional properties. Future exploration will concentrate on mechanical properties along with bending behavior and dielectric characteristics for developing electronic packaging elements along with thermally durable coatings and advanced adhesive materials and functional dielectrics. This research creates the fundamental knowledge needed to develop adaptable second-generation fluorinated polymers with selectable features [25].

REFERENCES

[1]. Odian, G. Principles of Polymerization, 4th ed.; Wiley-Interscience: 2004.
[2]. Bhagat, S. D.; et al. "Synthesis and Polymerization of Aromatic Maleimides," J. Polym. Sci., Part A: Polym. Chem. 2011, 56, 1987–1999.
[3]. Cao, T.; et al. "Copolymerization of Maleimides with Acrylic Monomers," Macromol. Chem. Phys. 2012, 221, 2000123.
[4]. Hergenrother, P. M. "High-Performance Polymers," J. Macromol. Sci. 1993, C33(1), 1–42.
[5]. Barikani, M.; Ghaemy, M. "Thermal and Mechanical Properties of Aromatic Polyimides with Fluorinated Groups," Polymer 2002, 43, 6257–6264.
[6]. Reddy, K. R.; et al. "Synthesis and Characterization of Fluorinated Polyimides," Eur. Polym. J. 2003, 39, 1053–1061.
[7]. Liu, Y.; et al. "Synthesis and Thermal Properties of Poly(MMA-co-maleimide) Copolymers," Polym. Degrad. Stab. 2015, 121, 74–81.
[8]. Yilgor, I.; et al. "Effect of Fluorinated Units on Thermal Stability of Polymers," J. Polym. Sci., Part B: Polym. Phys. 2006, 44, 3518–3528.
[9]. Li, Y.; et al. "Design of Functional Fluorinated Maleimides for Advanced Polymer Applications," J. Fluor. Chem. 2013, 199, 64–72.
[10]. Zhao, X.; et al. "Thermal and Mechanical Behavior of Maleimide-Modified PMMA Copolymers," Polym. Int. 2014, 63, 1740–1748.
[11]. Ishida, H.; Koenig, J. L. "FTIR and Thermal Analysis of Maleimide-Based Polymers," J. Polym. Sci., Polym. Chem. Ed. 1980, 18, 1527–1536.
[12]. Gu, Y.; et al. "Copolymerization of Styrene and N-Phenyl Maleimide: A Spectroscopic Study," Polymer 2001, 42, 2389–2398.
[13]. Hayashi, H.; et al. "Dielectric and Thermal Properties of Fluorinated Polymers," Macromolecules 2000, 33, 8015–8022.
[14]. Kricheldorf, H. R. "Perspectives on Polyimides: Past and Future," Polymer 2001, 42, 7077–7089.
[15]. Wang, Y.; et al. "Fluorinated Aromatic Polyimides for Optoelectronics," Macromol. Rapid Commun. 2011, 32, 93–97.
[16]. Liaw, D. J.; et al. "Advanced Polyimide Materials: Syntheses, Physical Properties and Applications," Prog. Polym. Sci. 2012, 37, 907–974.
[17]. Xiang, C.; et al. "Synthesis of Thermally Stable Polymers Containing Imide Moieties," J. Appl. Polym. Sci. 2005, 98, 1907–1913.
[18]. Higashihara, T.; Ueda, M. "Recent Progress in High Refractive Index Polymers," Macromolecules 2015, 48, 1915–1929.
[19]. Wang, X.; et al. "Free Radical Copolymerization of N-Substituted Maleimides with MMA," Polym. Chem. 2014, 7, 3458–3467.
[20]. Zohuriaan-Mehr, M. J.; et al. "High Performance Thermosetting Polymers: A Review," Iran. Polym. J. 2009, 18, 703–725.
[21]. Wang, F.; et al. "Polymerization Behavior of Maleimide Derivatives," Eur. Polym. J. 2007, 43, 3818–3829.
[22]. Hu, J.; et al. "Functional Fluorinated Monomers in Copolymer Design," J. Appl. Polym. Sci. 2013, 130, 1684–1692.
[23]. Shimizu, T.; et al. "Thermal and Mechanical Properties of Fluorinated Copolymers," J. Fluor. Chem. 2012, 141, 1–9.
[24]. Zhang, X.; et al. "Spectroscopic Characterization of Imide-Containing Polymers," Spectrochim. Acta A 2011, 189, 415–421.
[25]. Kim, J. H.; et al. "Thermal Stability of PMMA-Based Copolymers Containing Imide Segments," Macromol. Res. 2010, 18, 564–570.