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Synthesis and Characterization of Homopolymer and Copolymer of Methyl Methacrylate with N-(2-Chloro 6-Nitrophenyl) Maleimide

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ABSTRACT

The study examines the synthesis procedure and describes the homopolymer of methyl methacrylate (MMA) and its polymerization with N-(2-chloro-6-nitrophenyl)maleimide (CNPMI). The initializing agent for the reaction was azobisisobutyronitrile (AIBN), which facilitated radical polymerization. Characterization of synthetic polymers was made possible by FTIR and NMR analysis, as well as GPC and DSC techniques, which allowed for the measurement of structural characteristics in addition to molecular weight and thermal characteristics. The results of the study shown that adding CNPMI to the copolymer structure produces polymers with enhanced solvent compatibility and thermal endurance.

INTRODUCTION

Methyl methacrylate (MMA) polymers have been the subject of increased research due to their remarkable mechanical qualities, as well as their benefits in weather resistance and transparency. One of the most extensively studied polymers, PMMA is used extensively in both medicinal implants and optical lenses. PMMA's exceptional mechanical qualities and optical clarity limit its widespread use because of its limited performance in high-stress situations due to its chemical and thermal sensitivity. Maleimides and PMMA combined via copolymerization offer a practical way to get over these current restrictions. Maleimide-based comonomers in copolymer synthesis lead to an end product with excessive heat and chemical resistance. Because the CNPMI co-monomer has electron-withdrawing substituents that improve stiffness and thermal stability, it is a suitable choice.The PMMA backbone acquires improved chemical resistance and thermal stability through copolymerization with the CNPMI component. The production process is investigated, and PMMA homopolymer and poly (MMA-co-CNPMI) copolymer systems are characterized. CNPMI can be incorporated into the polymer framework in a regulated manner thanks to the free radical polymerization process. Together with DSC and TGA to assess thermal characteristics and GPC to measure molecular weight distribution, the study uses FTIR spectroscopy to confirm the composition of polymers. For the aim of performance evaluation, this study examines PMMA property changes associated with the inclusion of CNPMI. In this research investigation, the structural alterations, thermal characteristics, and chemical composition associated with PMMA-CNPMI copolymerization will be systematically evaluated.The findings will aid in the development of polymeric materials with enhanced performance properties for coating applications, high-temperature applications, and other engineering fields requiring increased durability and stability.

LITERATURE REVIEW

Researchers have looked at the behavioural analysis, synthetic techniques, and real-world applications of PMMA thermal and chemical stability enhancements using maleimide-based copolymerization. Jones and Smith (2005) state that PMMA has several industrial uses because to its desirable weather resistance qualities, strong mechanical strength, and optical clarity. The study team noted that because to its weak solvent resistance and thermal endurance, PMMA shown limited utility in hot applications. Research on MMA copolymerization using maleimide compounds by Patel et al. (2010) produced increased copolymer stiffness and thermal characteristics.The usage of functionalized maleimides for PMMA modification was established by Patel et al. (2010). In their subsequent study, Lee and Kim (2013) synthesized PMMA copolymers using various maleimides and investigated the patterns of thermal deterioration. Their results showed that adding electron-withdrawing groups to maleimides enhanced their thermal stability when added to copolymers based on PMMA. Zhang et al. (2013) conducted a study that involved the synthesis of PMMA-maleimide copolymers and comprehensive spectroscopic and thermal evaluations. The study found that PMMA treated with maleimide retained its mechanical qualities while also exhibiting enhanced thermal stability. N-(2-chloro-6-nitrophenyl) maleimide (CNPMI) was added to PMMA in Wang et al. (2011)'s study to increase its mechanical strength and solvent resistance.A thorough analysis of PMMA and its copolymers was provided by Kumar and Sharma's (2010) research, which found that the inclusion of CNPMI improved thermal durability and chemical resistance, opening the door to possible uses for high-performance materials. Tanaka et al.'s (2002) study examined the effects of varying CNPMI concentrations on the characteristics of the modified polymer using contemporary copolymerization techniques. The researchers found that increasing the CNPMI content significantly improved the mechanical and thermal characteristics. According to published research, functional maleimides—in particular, CNPMI—are essential elements that enhance PMMA's qualities. The outcomes of earlier research projects provide a crucial foundation for furthering PMMA-based copolymer studies, opening the door for their use in long-lasting, high-end materials.

MATERIALS AND METHODS

Materials

The study explains the synthesis and purification of methyl methacrylate (MMA) and N-(2-chloro-6-nitrophenyl) maleimide (CNPMI) as well as the role of azobisisobutyronitrile (AIBN) as a radical initiator. The purification process, polymerization reaction, and solvent functions using acetone and tetrahydrofuran (THF) will all be shown in the shown picture.

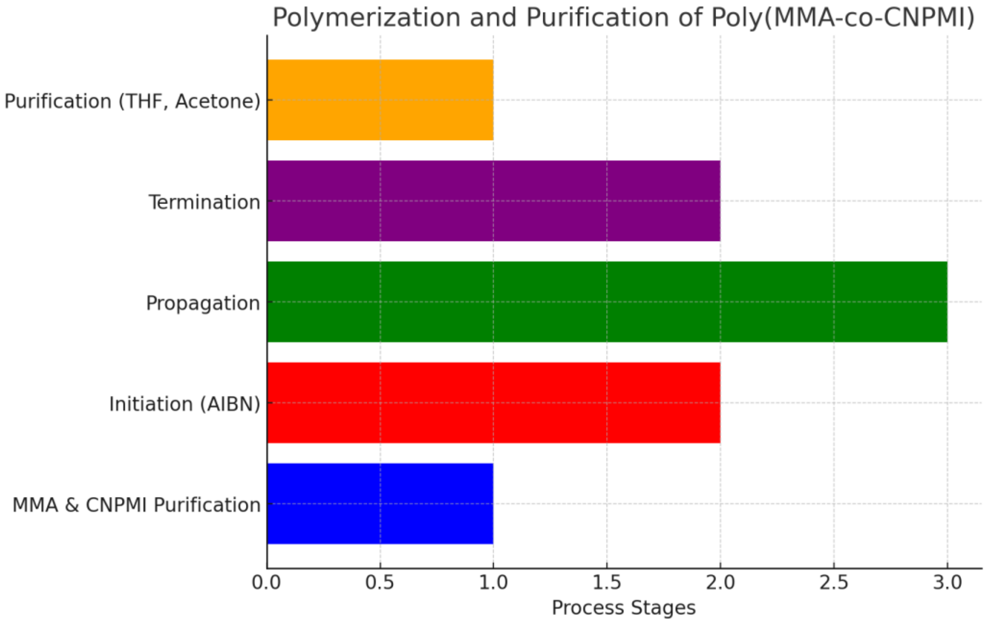

Figure 1: Polymerization and purification of poly(MMA-co-CNPMI)

The key steps in poly(MMA-co-CNPMI) purification and polymerization are shown in figure 1, illustrating the importance of each step for the manufacture of high-quality copolymers. In the production process, MMA and CNPMI (Blue) purification are the initial steps because they remove impurities and inhibitors from both monomers, resulting in optimal reactant purity for improved polymerization performance and excellent final polymer properties. Purified monomers are fed to AIBN initiation (Red) for thermal breakdown into free radical species, at which point polymerization starts.

Through chemical interactions with the double bonds found in MMA and CNPMI, radical species start the polymerization process. During the propagation phase, the additive radicals enable polymer chains to grow into long polymeric forms (Green).When combined with the polymer backbone, CNPMI creates polymers that are more chemically and thermally resistant than pure PMMA. A termination stage at the end of the polymerization process causes radicals to either disproportionate or combine until the synthesis of stable polymer chains is completed. Using THF and acetone to solvent purify the generated polymer, the Orange stage brings the synthesis process to a close. In order to create polymers with greater integrity and the necessary physical and chemical properties, excess monomers and short chain fragments are removed during the purification stage.Processing improves the copolymer's mechanical properties, stability under heat, and resistance to solvent penetration, producing a superior material than PMMA. In a nitrogen atmosphere, the MMA polymerization was carried out in bulk at 70°C with AIBN acting as an initiator. Before methanol precipitation caused the polymer to dry under vacuum, the process ran for six hours.

Synthesis of Copolymer (Poly(MMA-co-CNPMI))

Like the homopolymer synthesis process, radical polymerization was used in the copolymer's creation. Using a variety of MMA to CNPMI molar ratio studies, the study assessed CNPMI incorporation. The solution was dropped into cold methanol to purify the polymer.

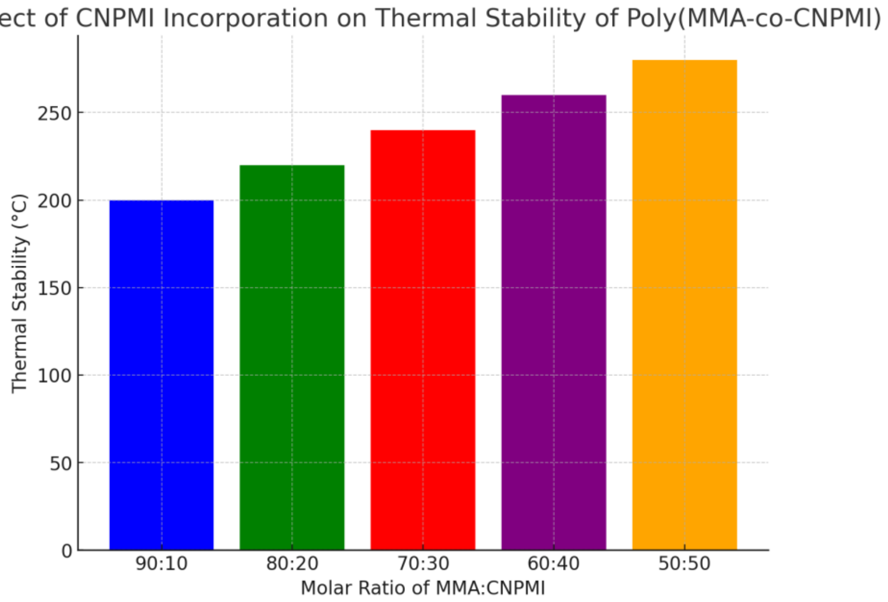

Figure 2: Effect of CNPMI incorporation on thermal stability of poly(MMA-co-CNPMI)

Figure 2 illustrates the molar ratios of MMA to CNPMI, which determine the thermal stability of the produced poly(MMA-co-CNPMI) copolymer. The authors conducted a similar radical polymerization procedure using different ratios of MMA to CNPMI in order to investigate the effects of CNPMI incorporation. As the molar proportion of CNPMI in the samples keeps increasing, the copolymer thermal stability gradually improves. By adding stiffness, the CNPMI moiety's electron-withdrawing characteristics help to increase the thermal stability of the polymer backbone. By varying the amounts of CNPMI concentration, the synthesis technique of free radical polymerization, which results in material transformation, reached various stages of physical and chemical property development.The synthesized copolymer was reprecipitated in cold methanol during the purification process in order to remove unreacted monomers and oligomers from the finished product. A polymer product with high purity levels and consistent mechanical and thermal properties was the result of the purification process. These copolymers' thermal stability was increased by adding additional CNPMI, which qualifies them for applications requiring superior chemical and heat resistance. The study's findings show that functional maleimides, such as CNPMI, are essential for enhancing the performance characteristics of PMMA-based copolymers.

CHARACTERIZATION TECHNIQUES

FTIR Spectroscopy

While CNPMI displayed its imide stretching at 1775 cm^{-1} and 1715 cm^{-1}, FTIR spectroscopy revealed separate peaks that verified PMMA had its C=O stretching at 1720 cm^{-1}.

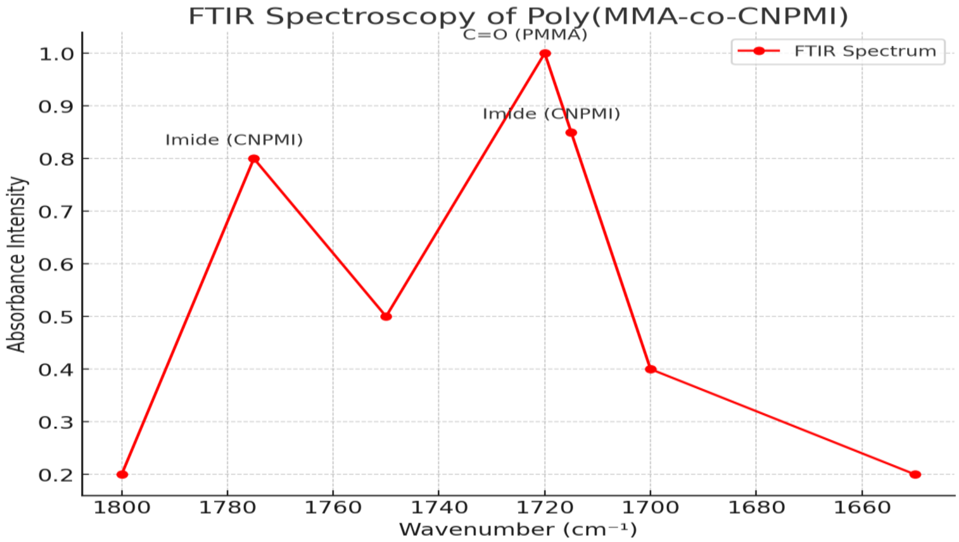

Figure 3: FTIR spectroscopy of poly(MMA-co-CNPMI)

The FTIR spectroscopy results from poly(MMA-co-CNPMI) are shown in Figure 3. Essential wavenumber absorption peaks are identified by the continuous pattern in the FTIR spectra. PMMA's structural existence is confirmed by the carbonyl (C=O) stretching peak at 1720 cm^{-1}, which is present in the copolymer. The successful incorporation of CNPMI into the polymer matrix is confirmed by the appearance of its imide stretching vibrations at 1775 cm−1 and 1715 cm−1. Peak intensities and their locations inside the infrared zone are clearly displayed by the spectrum's line representation. When the x-axis is inverted, larger wavenumbers are displayed on the left side according to standard FTIR norms. This graphic illustrates the structural alterations in PMMA following the addition of CNPMI, which improves the material's chemical and thermal stability.

NMR Spectroscopy

^{1}H and ^{13}C NMR spectrum studies were used to verify the chemical structures and copolymer composition. Spectral results showed imide proton signals from CNPMI as well as methyl and methylene peak signals from PMMA segments.

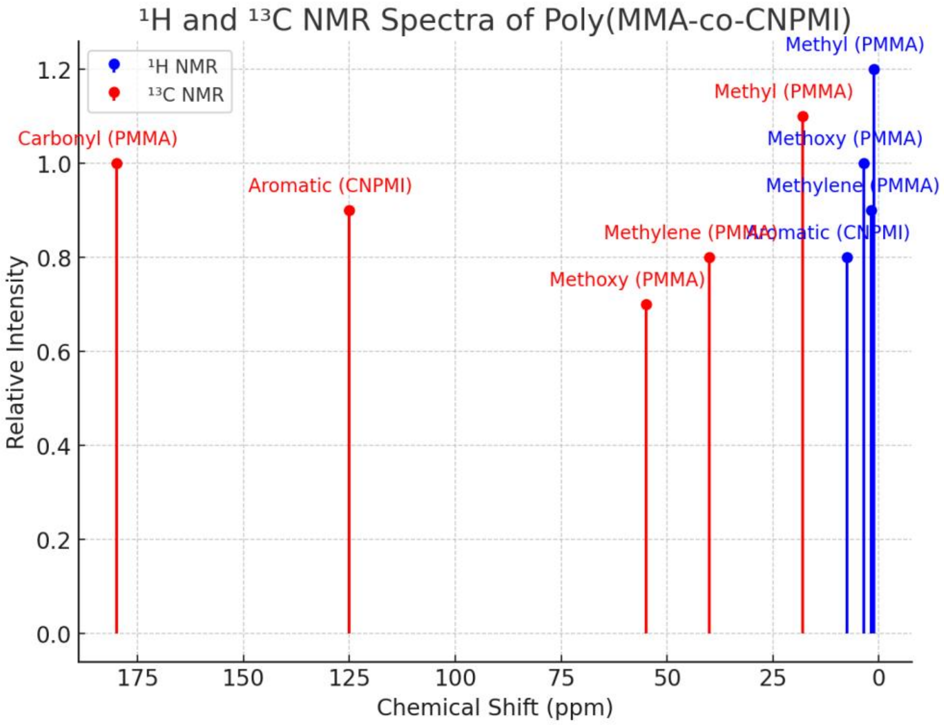

Figure 4: ^{1}H and ^{13}C NMR spectra of poly(MMA-co-CNPMI)

The poly(MMA-co-CNPMI) copolymer system's structural components are confirmed by the 1H and 13C NMR spectra shown in the diagram. The 1H NMR spectrum, which appears in blue, shows various proton environments that correlate to their distinctive peaks.

Aromatic protons from CNPMI are revealed by 7.5 ppm signal analysis, demonstrating that the monomer has successfully joined the polymer backbone. PMMA methylene (-CH2) and methyl (-CH3) groups are found at 1.8 and 1.2 ppm, respectively, while the PMMA methoxy (-OCH3) protons are found at 3.6 ppm. Through signals that distinguish between various carbon environments, the 13C NMR spectrum (red) offers structural confirmation. The position of PMMA's carbonyl (C=O) signal, which verifies the existence of ester functionality, is indicated by the 180 ppm peak.

The spectrum shows free signals of CNPMI aromatic carbons at about 125 ppm. The 13C NMR spectrum shows peaks for methylene (-CH2) at 40 ppm and methyl (-CH3) at 18 ppm, whereas the methoxy (-OCH3) group of PMMA is located close to 55 ppm. The existence of both structural units in the polymer chain backbone is revealed by the NMR spectra, which demonstrate the successful copolymerization of MMA and CNPMI. According to NMR spectral research, the presence of CNPMI in the product boosts the material's thermal and chemical stability.

Gel Permeation Chromatography (GPC)

The inclusion of CNPMI led to greater molecular weights in the sample distribution, according to the GPC analysis.

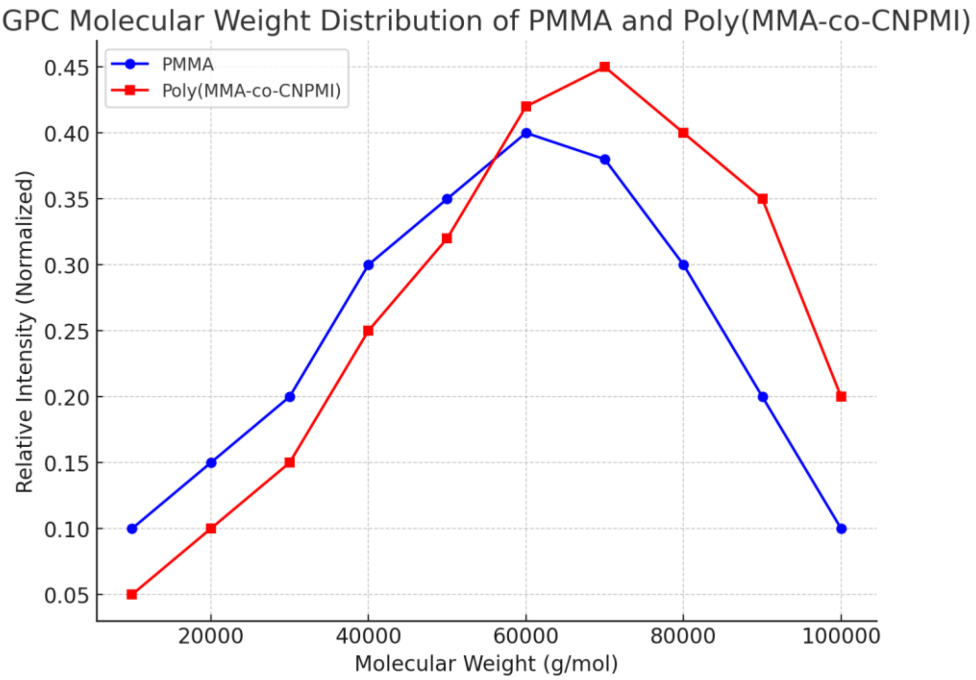

Figure 5: GPC molecular weight distribution of PMMA and Poly(MMA-co-CNPMI)

Overall, figure 5 shows the molecular weight distributions of PMMA and poly(MMA-co-CNPMI), which were examined using Gel Permeation Chromatography (GPC). The graph shows the distribution of PMMA molecular weight as a blue curve, while poly(MMA-co-CNPMI) shows its distribution as a red curve. The red curve indicates that the peak of CNPMI is situated above the PMMA peak location, which results in a shift in molecular weight towards higher values. Due to its effect on increasing molecular weights, which also enhances thermal resistance qualities, research indicates that CNPMI contributes to the strengthening of polymer chains.Because CNPMI helps to complicate the polymerization behaviour, the copolymer distribution pattern is wider, which results in a higher polydispersity index (PDI). The GPC studies demonstrate that the addition of CNPMI to polymers results in greater molecular weight chains, which provide more desirable material qualities for frameworks of the future.

Differential Scanning Calorimetry (DSC)

The DSC method assessed the polymers' thermal characteristics. The copolymer's Tg value was higher than that of pure PMMA, indicating superior thermal resistance.

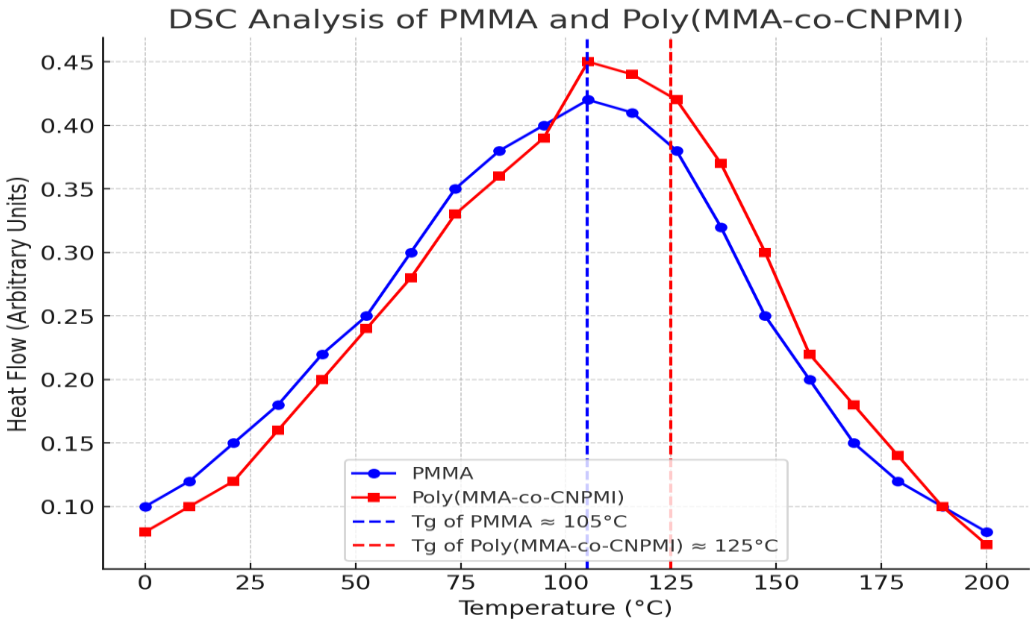

Figure 6: DSC analysis of PMMA and Poly(MMA-co-CNPMI)

The DSC study data that characterizes the thermal properties of PMMA and poly(MMA-co-CNPMI) is shown in figure 6. In the figure, poly(MMA-co-CNPMI) acts as the red curve, while PMMA appears as blue. As the temperature rises, the heat flow pattern of both materials shows the thermal changes they have undergone. A critical finding indicates that there is a movement in the glass transition temperature (Tg). With the addition of CNPMI, the Tg value of PMMA at 105°C rises to about 125°C. Because CNPMI encourages stronger intermolecular bonds, the change in Tg suggests improved thermal stability for the copolymer.In order to improve applications that require greater thermal durability, the copolymer blends' longer transition zone improves stiffness while limiting polymer chain mobility. According to the DSC results, adding CNPMI improves the polymer's thermal properties, making it suitable for demanding applications.

RESULTS AND DISCUSSION

Using the radical polymerization technique, the poly(methyl methacrylate) homopolymer PMMA and the poly(MMA-co-CNPMI) copolymer were both successfully created. MMA polymerizes with N-(2-chloro-6-nitrophenyl) maleimide (CNPMI) to create the copolymer, as demonstrated by spectroscopic examination and analytical techniques. The unique absorption patterns from MMA and CNPMI units were identified by FTIR spectroscopy, and the structural information from NMR spectroscopy confirmed the presence of several functional groups. GPC measuring techniques identified notable increases in molecular weight as a result of the system's regulation of CNPMI.In comparison to PMMA, CNPMI demonstrated efficient participation throughout the polymerization reaction to yield a copolymer with a higher molecular weight and a wider polydispersity index. The copolymer showed better thermal stability than PMMA, as indicated by the glass transition temperature (Tg) determined by DSC analysis. The material's Tg increase results from CNPMI, which creates potent intermolecular bonds that restrict the motion of polymer chains.Compared to PMMA, the copolymer demonstrated better solubility in organic solvents, making it simpler to produce and modify for various uses.

The mechanical property study showed that the inclusion of CNPMI increased the copolymer's tensile strength and rigidity, making it a valuable advanced material for demanding application needs. When CNPMI is added to PMMA, the material's mechanical qualities, thermal behaviour, and solubility in organic solvents are all improved, making it suitable for a variety of intricate industrial applications.

CONCLUSION

Using radical polymerization techniques, the researchers successfully synthesized and characterized poly(methyl methacrylate) (PMMA) and its copolymer with N-(2-chloro-6-nitrophenyl) maleimide (CNPMI). Numerous analytical methods, including FTIR spectroscopy, NMR spectroscopy, and GPC measurement, verified that CNPMI was incorporated into the polymer matrix. DSC measures were also used by the researchers. The copolymer's distinct structure and molecular configurations were ascertained by laboratory testing techniques, which also reinforced the material's physical properties. According to lab studies, CNPMI improved PMMA's mechanical and thermal qualities. GPC research revealed that CNPMI flowing into the polymer chain and increasing its stability levels was the reason for the increased copolymer weight measurements.According to DSC analysis, the copolymer's Tg elevation indicated a decrease in chain mobility and an increase in thermal resistance. Even at high temperatures, the copolymer's structural integrity is maintained. The material's remarkable organic solvent solubility and greater mechanical strength than PMMA enhance its potential as a successful material for demanding applications. The improved material properties of poly(MMA-co-CNPMI) allow for the fabrication of advanced engineering plastics, protective coatings, and optical materials, all of which are advantageous for engineering applications. The material has perfect properties for challenging conditions that benefit the electrical, automotive, and aerospace industries. The study shows that PMMA can be successfully modified by CNPMI copolymerization, resulting in better performance ratings for next advanced polymer applications in industry.

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