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| RESEARCH ARTICLE

Polymerization of N-phenylmaleimide Using Different Catalysts

Fiona Hammond Quarcoo[1] ✉ **Juliette C. N. Fouemina**[2] **and Gideon Appiah Kusi**[3]
[1]*College of Chemical Engineering, Nanjing Tech University, Nanjing Jiangsu 211816, China.*
[2]*School of Environmental and Safety Engineering, Jiangsu University, Zhenjiang Jiangsu 212013, China*
[3]*School of Economics and Management, Nanjing Tech University, Nanjing Jiangsu 211816, China*
Corresponding Author: Fiona Hammond Quarcoo, **E-mail**: fionaquarcoo@outlook.com

| ABSTRACT

The polymerization of N-phenylmaleimide (N-PMI) employing sodium phosphate tribasic as a catalyst has been successfully investigated in this study. The effect of dimethyl sulfoxide (DMSO) solvent on the principal catalyst, sodium phosphate tribasic, was extensively studied. The effects of several catalysts, including tetrabutylammonium acetate (TBAA), 4-dimethylaminopyridine (DMAP), Benzyl triethylammonium chloride (BTEAC), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1-Methylimidazole (1MA) and potassium phthalimide salt on polymerization of N-PMI have been discussed in this study. Additionally, the kinetics of polymerization in DMSO with Na_3PO_4 as the initiator is investigated. By using 1H and 13C nuclear magnetic resonance (NMR) spectrum analysis, attenuated total Reflection-Fourier transform infrared (ATR-FTIR), the resultant polymers were identified. Thermogravimetric and differential scanning calorimetric analyses were used to study the thermal behaviors. Our results prove that a salt form of catalyst can initiate the polymerization of N-PMI in dimethyl sulfoxide at a suitable concentration and under favorable conditions.

| KEYWORDS

Polymerization; catalysts; polymers

| ARTICLE INFORMATION

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1. Introduction

Polymaleimide (PMAI) can be defined as a type of high reactivity polymer often used as the polymer-based backbone of several functional materials with outstanding thermal stability. Ganjadhara et al. used PMAI to synthesize nonlinear optical structures as liquid crystals to improve their thermal properties (Zhang et al., 2011). For decades, N-phenylmaleimide (N-PMI) radical and anionic polymerization reactions have been thoroughly researched. Several catalysts or initiators used in polymerization have been studied. They include free-radical initiators (Cubbon, 1965), tert-butoxide potassium (Hagiwara, 1988), lanthanide complexes (Zhao, 2005), catalyst for rare-earth coordination (Lu, 2005), amines (Azechi, 2011), titanium nanocrystalline (Wang, 1999), organoaluminium initiators (Hagiwara, 1994), nonane 9-borabicyclo [3.3.1] (Kanno, 1997), thiophenol (Takeishi, 1992) and tertiary amines (Seris, 1993) or imidazole (Ivanov, 1984). The search for new catalysts or initiators, however, has continued due to the industry and commercial significance of the problems that previous studies on the solution polymerization of N-PMI had to deal with, such as yield losses, low molecular weights, long response times, lack of solvents, catalyst removal from resultant polymers, and extreme conditions (in the dark, under nitrogen atmosphere, or at -78 °C) (Okamoto, 1991). Previous studies had only made mentioned how fluorides were used as initiators in the polymerization of maleimides (Wu, 2020). However, all the forms of polymerization performed with maleimides have either been anionic or radical polymerization. In this study, we investigate the use of some salts in the polymerization reaction. Herein, we employ several organocatalysts as well to initiate the polymerization of N-PMI.

Sodium phosphate tribasic is one of the most versatile compounds which has been employed as water softeners, boiler-water additives, detergents, and metal cleaners. It is also applied in textiles and paper manufacturing, laundering, tanning, sugar purification, photographic developers, paint removers, industrial cleaners, dietary supplements, buffers, emulsifiers, and food additives. Sodium tribasic phosphate has been found to be a crucial initiator in polymerization reactions. It has been employed in several organic reactions as a catalyst. In a study conducted by Paolo De Filippis, anhydrous sodium phosphate was used to catalyze rapeseed oil transesterification and biodiesel production (Jiang, 2010). One advantage is that it can easily be recovered and reused. Recently, a study was conducted using fluoride ions as an initiator in polymerizing N-PMI. As a catalyst, the fluoride anion can speed up a variety of reactions, including the alkylation and arylation of phenols, catechols, alcohols (Gangaram, 2013), and other compounds, the Michael addition reaction, esterification reactions (Ooi, 2011), Knoevenagel reactions (Yu, 2013), aldol condensations, intramolecular cyclization reactions (Bhalla, 2010), oxidations, nucleophilic fluorination reactions (Evano, 2018), multicomponent reactions (Gao, 2008), and some specific polymerizations (Zheng, 2019). Fluoride ions are usually utilized in numerous chemical processes as a base, an oxidant, or a nucleophile (Bozdemir, 2010). However, when utilized in polymerization operations, acid and base catalysts have some downsides. One significant negative is that they eventually end up being neutralized at the end of the reaction, making the catalyst unusable and challenging to recover a pure product. Herein, we sought to look for an alternative way to overcome this major problem (Li, 2004).

In this study, we investigate the polymerization of N-PMI with sodium phosphate tribasic (Na_3PO_4) as well as eight other catalysts in dimethyl sulfoxide (DMSO). High yields of poly(N-PMI)s with exceptional thermal stability were produced with Na_3PO_4. Importantly, this is the first ever conducted experiment on polymerization of N-PMI using sodium phosphate tribasic as a catalyst.

2. Materials and Method

2.1. Materials and Equipment

Sodium phosphate tribasic (Na_3PO_4) and dimethyl sulfoxide (DMSO) were purchased from Energy Chemical Reagent Co., Ltd. DBU was purchased from Macklin Reagent Co., Ltd. All other reagents were purchased from Aladdin Chemical Reagent Co., Ltd. All chemicals were used without further purification. Deionized (DI) water with a resistivity of ≥ 18.2 MΩ∗ cm was used throughout the experiments. Nuclear Magnetic Resonance spectra (1H and 13C NMR) were recorded on a Bruker 500 MHz instrument, and chemical shifts were calculated in ppm () in reference to internal tetramethyl silane (0 ppm) and dimethyl sulfoxide-d6 (25 ppm), respectively, for 1H and 13C NMR. A nitrogen-filled Mettler Toledo DSC 1 machine was used to study differential scanning calorimetry (DSC). Using a Mettler-Toledo TGA/DSC 1 LF apparatus and a heating rate of 10 °C min-1 up to 800 °C, a thermogravimetric analysis (TGA) was carried out in nitrogen.

2.2. Polymerization methods of N-PMI

Catalyst Test: The catalyst (0.02 mmol) was added to a DMSO (2 mL) solution containing N-PMI (173.17 mg, 1 mmol) in an air-filled 2 mL clear glass bottle with a magnetic stirrer. The reaction mixture was agitated for 0.5 hours at room temperature before reacting in quartz sand at 80 °C for 48 hours. After the reaction was finished, the solution was precipitated dropwise in methanol containing a little amount of HCl and agitated for 2 hours. The resultant solid was filtered off, washed with DI water, methanol, and acetone/hexane 1:1 (v/v) sequentially, then dried at 80 °C under vacuum to produce a light brown powder.

Optimum catalyst dosage: Following the identification of the catalyst, various concentrations of Na_3PO_4 (0.001, 0.005, 0.01, 0.02, 0.05 mmol) were added to a solution of DMSO (2 mL) containing N-PMI (173.17 mg, 1 mmol), and the mixture was then allowed to react for 0.5 hours at ambient temperature and 48 hours at 80 °C. The mixture was stirred for two hours while being precipitated in methanol that contained a minimal amount of HCl. The final polymer product was obtained by filtering the produced material, washing it with DI water, methanol, and acetone/hexane 1:1 (v/v), and then drying it at 80 °C under a vacuum. Table 2-2 displays the outcomes.

Kinetic study: N-PMI (692.68 mg, 4 mmol), DMSO (6 mL), and Na_3PO_4 (6.56 mg, 0.04 mmol) were all combined in a 10 mL transparent glass bottle. After 0.5 hours of at-room-temperature reaction, the mixture was heated to 60 °C to begin the polymerization process. In order to precipitate the polymer, 500 L of the reaction solution were taken out at intervals of (0.5 h, 1 h, 1.5 h, 2 h, 2.5 h, 3 h, 5 h, 10 h, 24 h, and 48 h) and added dropwise to methanol with a little amount of HCl. The final powdered product was filtered out, repeatedly rinsed with DI and methanol, and then dried under vacuum at 80°C to a consistent weight. Gravimetric calculations were also used to convert the units.

3. Results and Discussion

3.1. Effect of various catalysts on polymerization of N-PMI in DMSO

There is evidence from several research that various catalysts can cause N-PMI to polymerize. We investigated the polymerization potential of N-PMI using nine organocatalysts by incubating the compound in DMSO for 0.5 hours at ambient temperature and 48 hours at 80 °C, respectively. 0.02 mmol of each catalyst was used in the polymerization process. DMSO was chosen because it is a strong solvent for the dissolution of difficult monomers and preservation of high molecular weight polymers in solution. This particular solvent is non-toxic and has a low odor.

The solution of N-PMI in DMSO turned red when TBAA, DMAP, DBN, DBU, DABCO, and potassium phthalimide salt were added at ambient temperature. BTEAC, 1MA, and Na_3PO_4 were added, but the solution remained pale yellow. This may be because of their insufficient solubility in DMSO at ambient temperature. The polymerization reaction then commenced as soon as the reaction mixture reached 80 °C. After starting out red, the solution's color progressed to deep red and then black red. Table 2-1 and Figure 2-1 present a summary of the polymerization results.

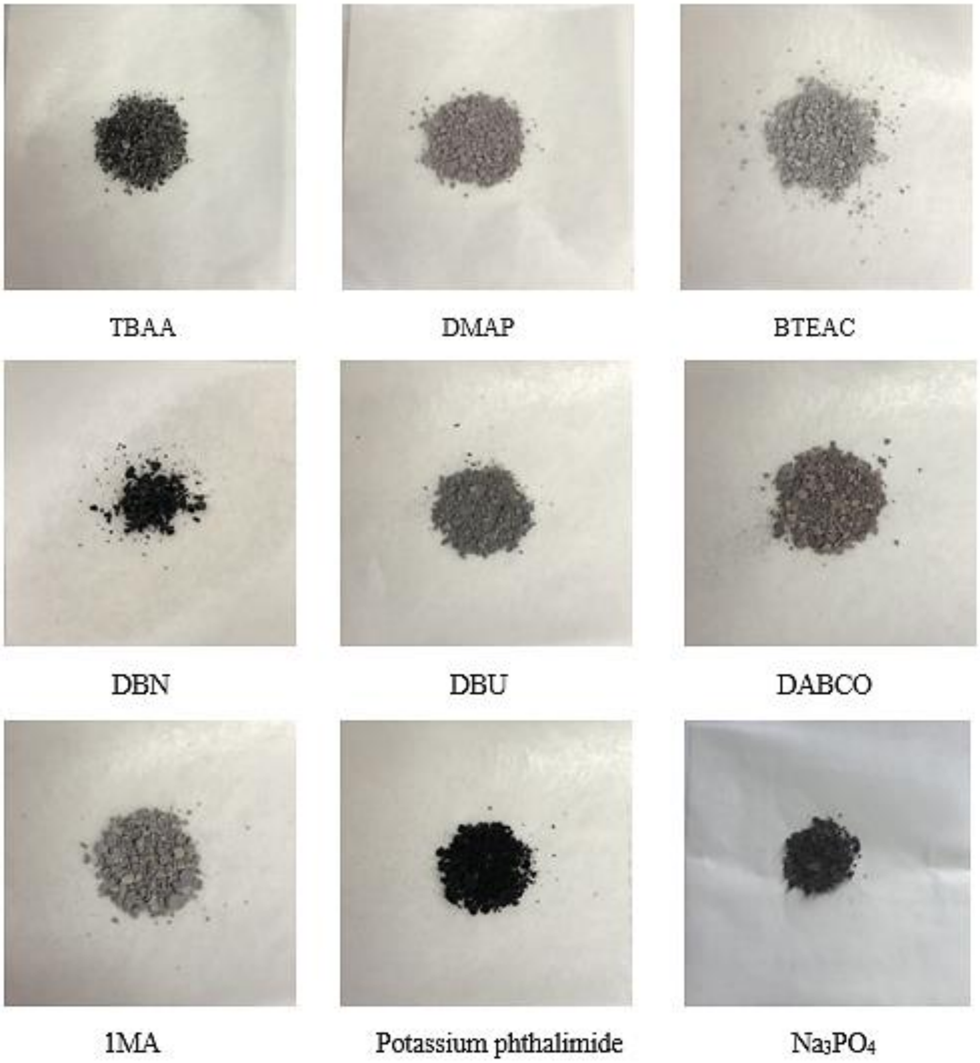
When TBAA was used as a catalyst, a dark-colored powder was obtained in a small yield (43%), as seen in Figure 2.1. DMAP, which was also used in polymerizing the monomer, yielded a grey-colored powdered polymer material. BTEAC catalyzed N-PMI to give a light gray powdered material in smaller yields of 67%, similar to that of DMAP (69%). DBN catalyzed N-PMI to give a darker powdered material after participating in the reaction. Comparing DABCO to DBU, the yield was almost the same for both catalysts. There was not much difference in color and morphology of the obtained polymer. 1MA, as it reacted with the monomer, yielded similar powdered material as that of BTEAC. Last but not least, the potassium phthalimide catalyst produced a black-colored powder with 81% yield. Even though only 0.02 mmol of Na_3PO_4, the main catalyst in this reaction method, was used, it turned out to have the highest yield. Na_3PO_4 had the highest activity in terms of catalyzing the polymerization of N-PMI among these nine catalysts because it produced poly(N-PMI) with the highest yield.

3.2. Effect of different amounts of Na_3PO_4 on polymerization of N-PMI in DMSO

Following the confirmation that Na_3PO_4 would work as the catalyst, various doses of Na_3PO_4 (0.001, 0.005, 0.01, 0.02, 0.05 mmol) were added to the reaction solution. The conversion rate is shown in Table 2-2. The outcomes demonstrate that the catalyst's dosage has an impact on the polymer yield. A light-yellow powder was produced with the lowest yield (69%), as shown in Table 2.2 and Figure 2.2, when 0.001 mmol Na_3PO_4 was employed to catalyze the polymerization of N-PMI. Afterward, the yield of the produced polymer rapidly declined as the Na_3PO_4 dosage was increased. The yield of polymers catalyzed by 0.02 mmol Na_3PO_4 was 83%, but the yield of polymers catalyzed by 0.05 mmol Na_3PO_4 was only 80%. In conclusion, the maximum yield was produced by polymerizing N-PMI using 0.01 mmol Na_3PO_4.

Table 2- 1. Polymerization of N-PMI (1 mmol) with different catalysts (0.02 mmol) in DMSO

Run	Catalyst	Yield (%)
1	TBAA	43
2	DMAP	69
3	BTEAC	67
4	DBN	70
5	DBU	30
6	DABCO	30
7	1MA	44
8	Potassium phthalimide	81
9	Na_3PO_4	83



TBAA DMAP BTEAC

DBN DBU DABCO

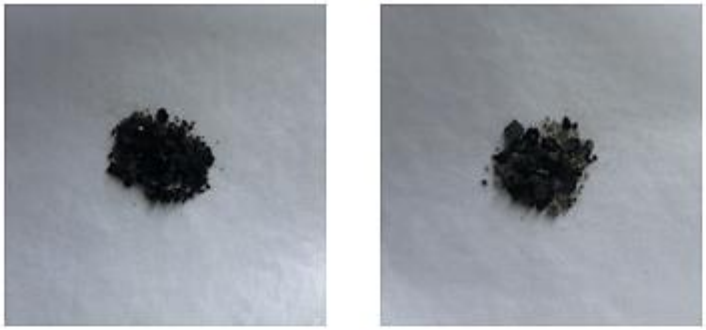
1MA Potassium phthalimide Na_3PO_4

Figure 2- 1: Products obtained by polymerization of different catalysts and N-PMI in DMSO

Table 2- 2. Polymerization of N-PMI (1 mmol) with different doses of Na_3PO_4 in DMSO

Run	Na_3PO_4 (mmol)	Yield (%)
1	0.001	69
2	0.005	76
3	0.01	86
4	0.02	83
5	0.05	80

Na_3PO_4(0.001 mmol) Na_3PO_4(0.005 mmol) Na_3PO_4(0.01 mmol)



Na_3PO_4(0.02 mmol) Na_3PO_4(0.05 mmol)

Figure 2- 2: The product obtained by polymerization of different doses of Na_3PO_4 and N-PMI in DMSO.

3.3 Polymerization kinetics and mechanism

Na_3PO_4 was used as a catalyst, and the polymerization kinetics were determined. Figure 2-3 shows that the conversion increased with the duration of the polymerization process. Thus, extending the polymerization process increases the yield. The rate of polymerization obviously increased over the first 90 minutes before steadily declining afterward. The rate may have decreased due to a reduction in monomer concentration. In addition, the diffusion of low-molecular-weight oligomers to the propagation species is insufficient due to the rise in the viscosity of the polymerization solution.

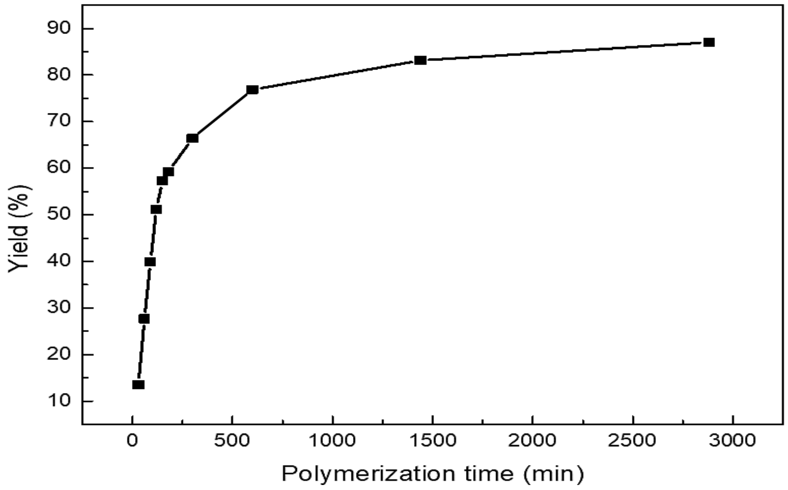


Figure 2- 3: Effect of polymerization time on yield (692.68 mg N-PMI and 0.04 mmol of Na_3PO_4 dissolved in 6 mL DMSO, temperature = 60 °C).

3.4 Characterization of polymers

First, the polymer produced when Na_3PO_4 is used as a catalyst in DMSO was characterized using 1H NMR, 13C NMR, and attenuated total reflection-Fourier transform infrared (ATR-FTIR). Figure 2.4 display a 1H NMR of the polymer. A wide bump between 6 and 8 ppm indicates the presence of the phenyl group. The methine group signal appears as a wide bump between 3 and 5 ppm. The peak assignments are consistent with the 5:2 ratio of phenyl hydrogen atom integration to methane hydrogen atom integration. The polymer is also subjected to 13C NMR characterization. Figure 2.5 displays the final outcome. The carbonyl carbons are assigned a small broad bump at 177 ppm. The three minor peaks at 125–134 ppm are attributed to the polymer's phenyl carbons. The methine carbons in the polymer chain are responsible for the weak and widened signal that was seen between 38 and 42 ppm, close to the signal of DMSO carbons. The results of the 1H and 13C characterization are comparable to those of the earlier study using fluorides.

Figure 2.6 displays the ATR-FTIR spectra of the PMI monomer (Curve A) and the resultant poly(PMI) (Curve B) in the Na_3PO_4/DMSO system. Multiple color bars have been used to indicate the areas where the poly(PMI) and N-PMI monomer IR spectra differ. The typical imides functional group peaks in the polymer (Spectrum B) at 1703, 1188, and 733 cm^{-1} are wider than equivalent bands in the monomer (Spectrum A). However, the strong vinyl CH characteristic peak at 840 cm^{-1} is nearly nonexistent, demonstrating the addition polymerization of the vinyl. Thermogravimetric analysis (TGA) with nitrogen as the protective gas was performed in order to determine the thermal stability of the resulting polymer using Na_3PO_4 as a catalyst. The thermal decomposition of the resulting polymer using Na_3PO_4 in DMSO is illustrated in Figure 2.7. It can be seen that the main weight loss of the obtained poly(PMI) took place around 450 °C. This temperature was not so different from the one observed in the previous study. The resultant polymer showed remarkable thermal stability when the Na_3PO_4/DMSO system was utilized. The polymer produced at 500 °C had a char yield of about 26%. TGA findings indicate that Na3PO4 is an excellent catalyst for N-PMI polymerization using DMSO as the solvent.

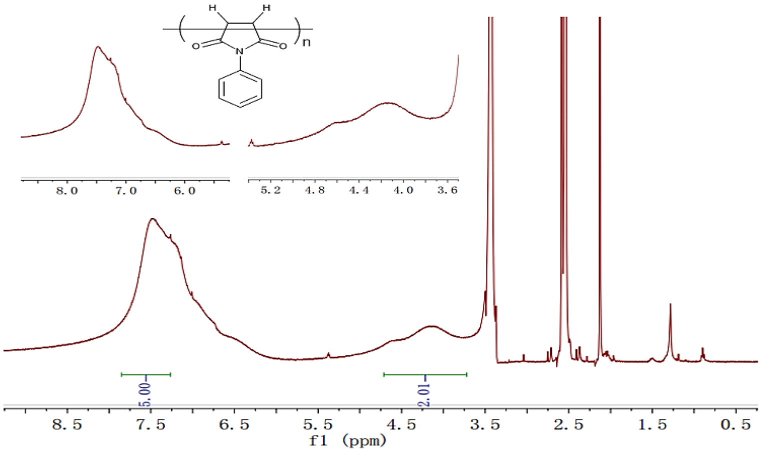


Figure 2- 4: ^{1}H NMR spectrum of the poly(N-PMI) in DMSO-d_6

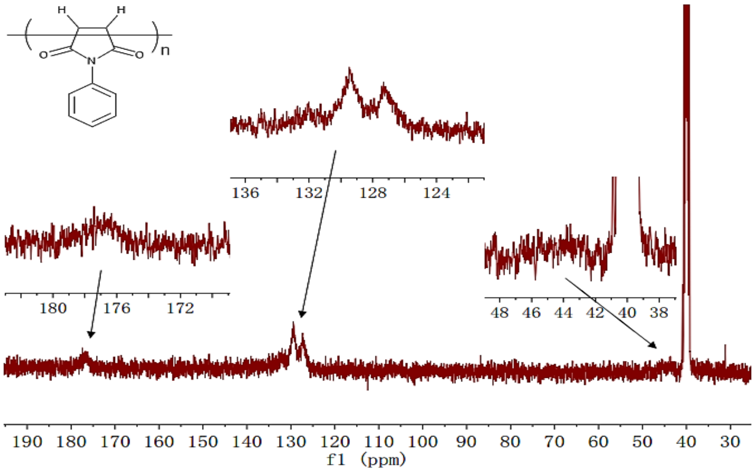


Figure 2- 5: ^{13}C NMR spectrum of poly(N-PMI) in DMSO-d_6

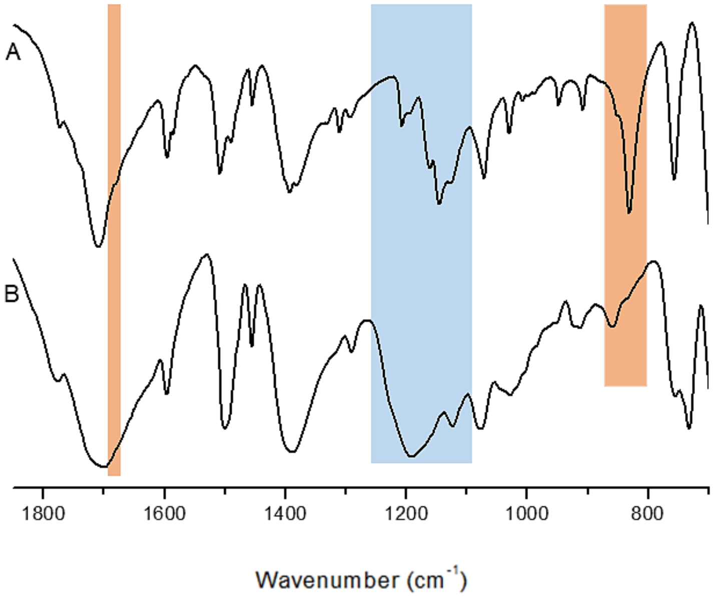


Figure 2- 6: ATR-FTIR spectra of N-PMI (curve A) and poly (N-PMI) (curve B)

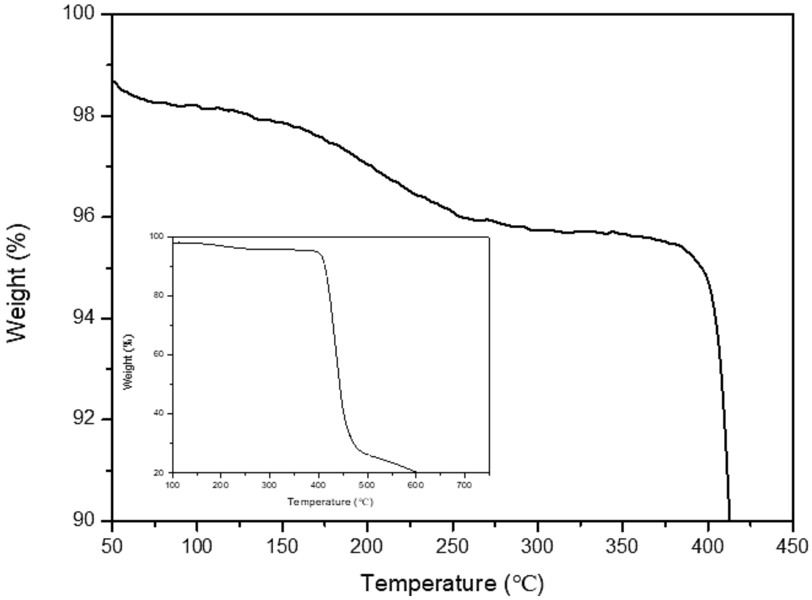


Figure 2- 7: TGA thermograms of poly(N-PMI)

3.5 DSC Studies of Polymers

Figure 2-8 shows the DSC thermograms of the polymers obtained by using the Na_3PO_4/DMSO system to catalyze N-PMI and N-MMI (N-Methylmaleimide), respectively. After heating them to 300 ℃ at a rate of 10 ℃/min, probably due to melting, the poly(PMI) had a wide endothermic transition between 36.01 ℃ and 88.08 ℃ with an enthalpy value of 42.428 J/g. In addition, the poly(MMI) had a wide endothermic conversion between 44.12 ℃ and 98.50 ℃ and between 131.06 ℃ and 193.30 ℃, and the enthalpy values were 105.594 J/g and 34.004 J/g, respectively. However, no significant glass transition was observed for these polymers.

Figure 2-9 shows the DSC thermograms of the mixture of Na_3PO_4 and BMIs (bismaleimide) at different heating rates. When scanning at a rate of 2.5 ℃/min, the polymer had three endothermic transitions at 42.62 ℃-72.93 ℃, 152.73 ℃-157.73 ℃, and 163.42 ℃-165.24 ℃ respectively. When scanning at a rate of 5 ℃/min, in addition to the three endothermic transitions at 48.94 ℃-164.53 ℃, there was a wider exothermic transition at 168.43 ℃-207.02 ℃, which may be due to crystallization. When scanning at the speeds of 10 ℃/min and 20 ℃/min, there were only two endothermic transitions due to melting at 63.19 ℃-160.72 ℃, and one exothermic transition due to crystallization at 171.92 ℃ -257.64 ℃.

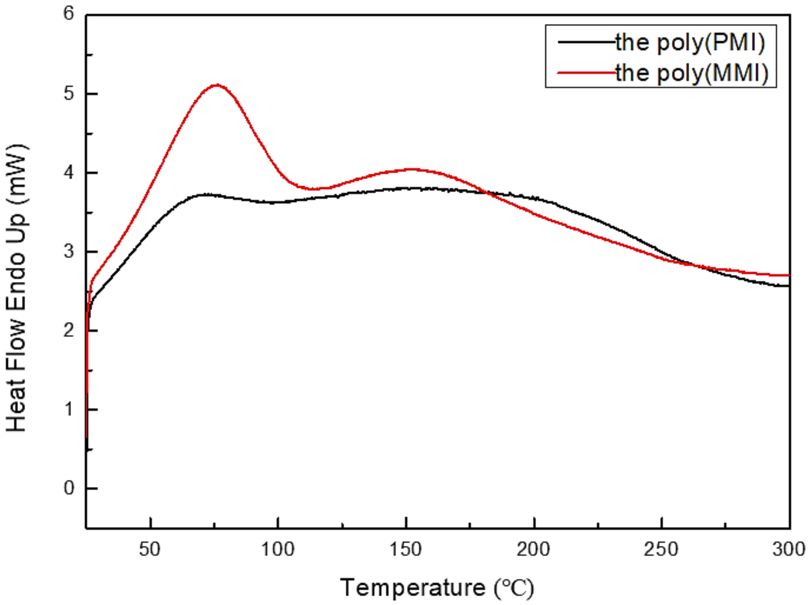


Figure 2- 8: DSC thermograms of poly(N-PMI) and poly(N-MMI)

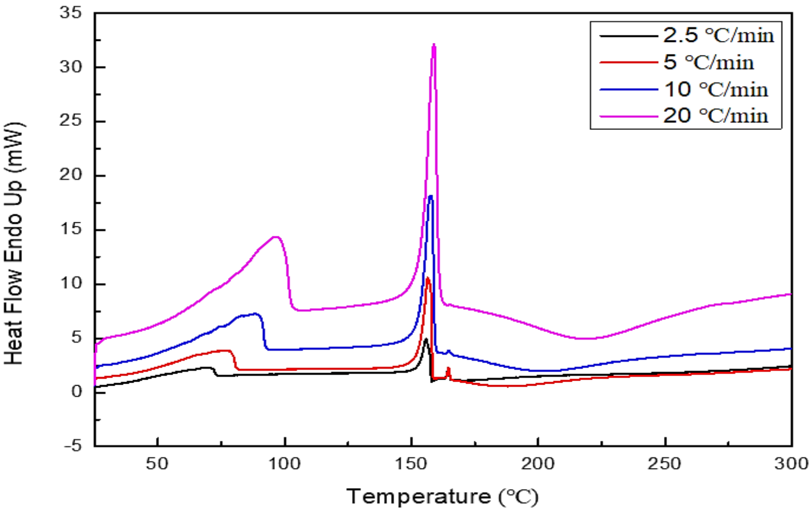


Figure 2- 9: DSC thermograms of the mixture of Na_3PO_4 and BMIs at different heating rates

4. Conclusion

A systematic investigation of the N-PMI polymerization with Na_3PO_4 as a catalyst has been made. Na_3PO_4 can efficiently start the polymerization of N-PMI in DMSO under relatively moderate circumstances, producing poly (PMI) with good thermal stability and outstanding yields. Our results suggest that the high processing temperature of bismaleimide and maleimide resins can be reduced by utilizing Na_3PO_4 as a catalyst in the solution for efficient polymerization. Additionally, our findings will encourage the use of bismaleimide and maleimide resins in machinery, electronics, aerospace, and other industrial domains.

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Conflicts of Interest: The authors declare no conflict of interest.

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