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Synthesis of new maleimide monomers and their copolymerization

B.L. Hiran*, Shivira Bapna*, Divya Singh and Sapna Jain

Chemical Kinetics and Polymer Research Laboratory, Department of Chemistry, University College of Science, Mohanlal Sukhadia University, Udaipur (Raj.), INDIA

ABSTRACT

Two new maleimide monomers of 2,4-dimethylbenzene-1-amine and 2,6-dimethylbenzene-1-amine (P24PMI and P26PMI respectively) were synthesized using maleic anhydride, P_2O_5, concentrated H_2SO_4 and DMF as a solvent. Both maleimide monomers were copolymerized with each other using azobisisobutyronitrile (AIBN) as free radical initiator. Monomers and copolymer formation were confirmed by FT-IR and ^{1}H-NMR spectral analysis. Monomers were also confirmed by elemental analysis. Solubility behaviour of monomers and copolymer was also studied.

Keywords: 2,4-Dimethylbenzene-1-amine, 2,6-Dimethyl benzene-1-amine, copolymerization, spectral analysis.

INTRODUCTION

Polyimides cover the whole range of high performance polymer. They are a sophisticated family of materials, which have applications in highly technical end use fields from aerospace to microelectronics [1-3]. Polyimides are in the limelight as replacement for epoxies and also attracting the aerospace market [4-6]. Their diversity is such that it leads them into applications as fibers, films, coatings and composite prepares where their major advantage, a high resistance to heat, places them in a niche other polymer can't enter [7-9].

From literature survey it seems huge applications of polyimides in various fields, we have synthesized a new polyimide that may have many applications in various fields.

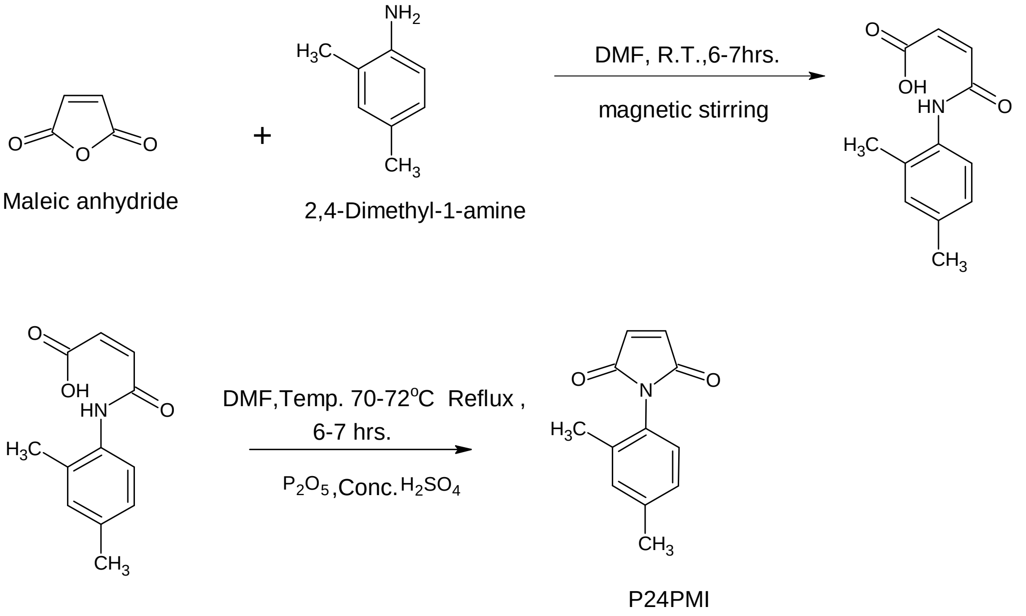
MATERIALS AND METHODS

Materials

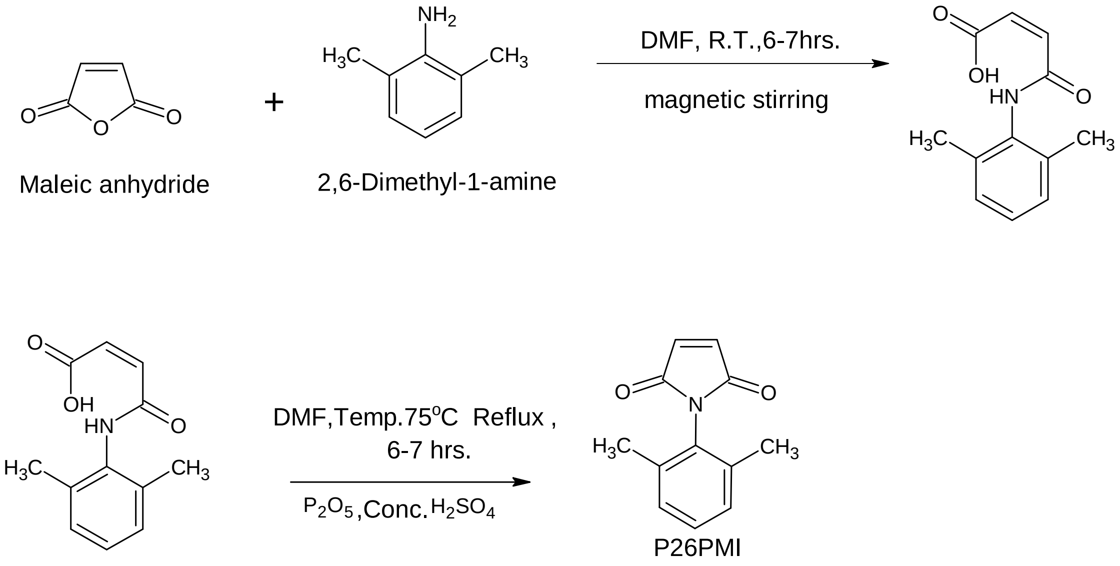
2,4-Dimethylbenzene-1-amine and 2,6-dimethylbenzene-1-amine used were of analytical grade (Loba Chem. Pvt. Ltd.). Maleic anhydride, Azobisisobutyronitrile (AIBN), phosphorous pentoxide and concentrated H_2SO_4 were used as received. N, N'-Dimethylformamide (DMF) was used after distillation.

Method

Monomers preparation (Scheme 1&2): The solution of maleic anhydride (9.81 gm, 0.1 mol) in DMF was gradually added to a solution of 2,4-dimethylbenzene-1-amine or 2,6-dimethylbenzene-1-amine (12.4 ml, 0.1 mol) in 25ml DMF. This reaction mixture was stirred at room temperature for 6-7 hrs. Then 7 to 7.5 gm P_2O_5 and 5 drops concentrated H_2SO_4 were added and again stirred for 6-7 hrs continuously at 70-75°C. The resulting solution was poured into a beaker containing crushed ice-water to precipitate 2,4-dimethyl (phenyl) maleimide monomer (P24PMI) or 2,6-dimethyl (phenyl) maleimide monomer (P26PMI) respectively. The compounds were characterized by FT-IR and ^{1}H-NMR and elemental analysis. P24PMI and P26PMI were crystallized with carbontetrachloride and methanol respectively. Melting point of P24PMI and P26PMI was found 54°C and 92°C respectively.

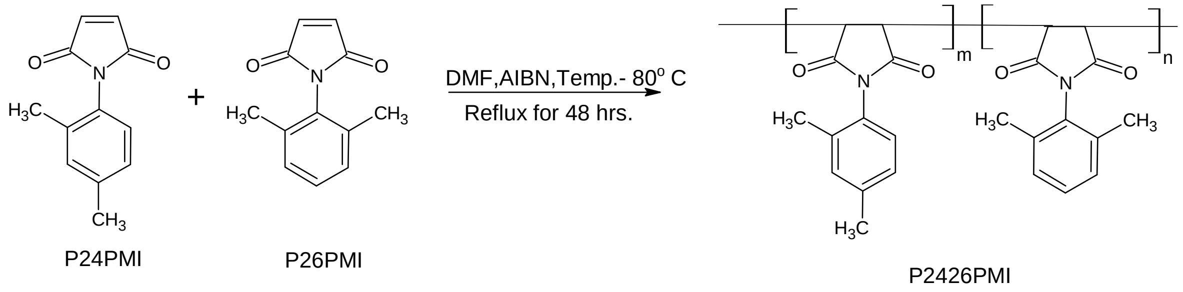


Scheme 1



Scheme 2

Copolymer preparation (Scheme 3): Weighed amount of P24PMI (2.01 gm) and P26PMI (2.01 gm) were introduced into a three-necked round bottom-flask with free radical initiator AIBN (150 mg). DMF was used as solvent. This reaction mixture was refluxed at 80°C for 48 hrs. The reaction mixture was poured in 10% methanol water mixture after polymerization for a given time, to precipitate copolymer P2426PMI. P2426PMI was crystallized from methanol. Synthesis of P2426PMI was confirmed by FT-IR and ^{1}H-NMR spectral analysis.



Scheme 3

RESULT AND DISCUSSION

Solubility

Relative solubility of monomers and copolymer in various polar and non-polar solvents have been summarized in Table 1.

Table 1: Solubility of monomers P24PMI, P26PMI and copolymer P2426PMI

Solvent	P24PMI	P26PMI	P2426PMI
Acetone	S	S	S
Ethanol	S	S	S
DMF	S	S	S
THF	S	S	S
Nitrobenzene	S	S	S
Benzene	S	S	PS
CH_2Cl_2	S	S	S
CCl_4	S	PS	PS
Ether	S	S	PS
Methanol	S	S	S
1,4-Dioxan	S	S	S
Water	IS	IS	IS
CH_3COOH	S	PS	PS
Cyclohexane	PS	PS	PS
Cyclohexanone	S	S	S
CS_2	S	S	PS
DMSO	S	S	S

S = Soluble, PS = Partially soluble, IS = Insoluble

Table 1 show that both monomers (P24PMI and P26PMI) show good solubility behaviour in various solvents and copolymer P2426PMI shows average solubility behaviour. All three synthesized compounds are insoluble in water.

Elemental analysis

Synthesis of P24PMI and P26PMI was confirmed by elemental analysis. Elemental analysis was made on Carlo-Erba Model NA500 Series analyzer. Carbon, nitrogen and hydrogen elemental analysis support the synthesis of P24PMI and P26PMI. Table 2 shows the theoretical and experimental percentage values of the elements.

Table 2: Percentage of C, N, H in P24PMI AND P26PMI

	Element	**C**	**N**	**H**
P24PMI Monomer Monomer	Theoretical %	71.64	6.96	5.47
	Experimental %	72.88	7.35	4.32
P26PMI Monomer Monomer	Theoretical %	71.64	6.96	5.47
	Experimental %	69.88	6.15	4.99

FT-IR Spectral Analysis (Figure 1, 2&3)

FT-IR spectra of samples were recorded on Perkin-Elmer spectra RXI (4000–450 cm^{-1}) FT-IR spectrophotometer using KBr pellet technique. FT-IR spectra of the monomers (P24PMI and P26PMI) and copolymer P2424PMI showed the following absorption bands that have been summarized in Table 3 & 4, respectively.

Table 3: FT-IR absorption bands of P24PMI and P26PMI

Type of vibrations	**P24PMI IR (CM^{-1})**	**P26PMI IR (CM^{-1})**
Ar C–H stretching	3022.5	3024.2
Trisubstituted phenyl ring	829.3, 877.3	827.9, 948.6
Ar C=C stretching	1590.2	1595.8
Ar C–N stretching	1390.6	1379.8
C=O sym. and asym. stretching of imide ring	1716.2 & 1781.2	1716.5 & 1775.2
C=C stretching of imide ring	1616.2	1636.3
=C–H stretching of imide ring	3102.5	3101.3
C–H stretching of methyl group	2925.7	2927.0

Table 4: FT-IR absorption bands of P2426PMI

Type of vibrations	**P2426PMI IR (CM^{-1})**
Ar C–H stretching	3021.6
Trisubstituted phenyl ring	827.9, 948.6
Ar C=C stretching	1506.4
AR C–N stretching	1215.3
C=O sym. & asym. stretching of imide ring	1714.5 & 1780.2
C–C stretching of imide ring	2927.2
–C–H stretching of imide ring	1447.2
C–H stretching of methyl group	2866.6

FT-IR absorption bands in Table 3 & 4 confirm the synthesis of monomers, copolymer and their structure. Table 4 also confirms the synthesis of copolymer P2426PMI as C=C stretching of imide ring of P24PMI and P26MI (at 1616.2 and 1636.2 CM^{-1} respectively) and =C–H stretching (3102.5 and 3101.3 CM^{-1}) disappeared upon polymerization and two new peaks were found at 2997.2 and 1447.2 CM^{-1} (C-C and -C–H stretching respectively.

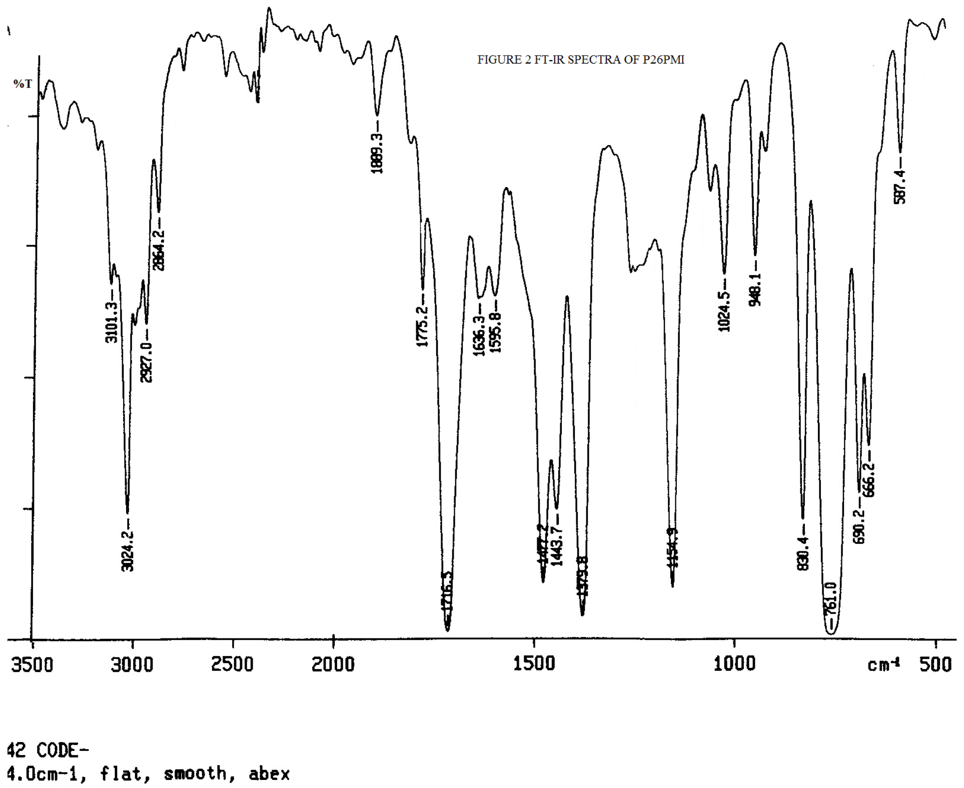


Fig. 1: FT-IR spectra of P24PMI

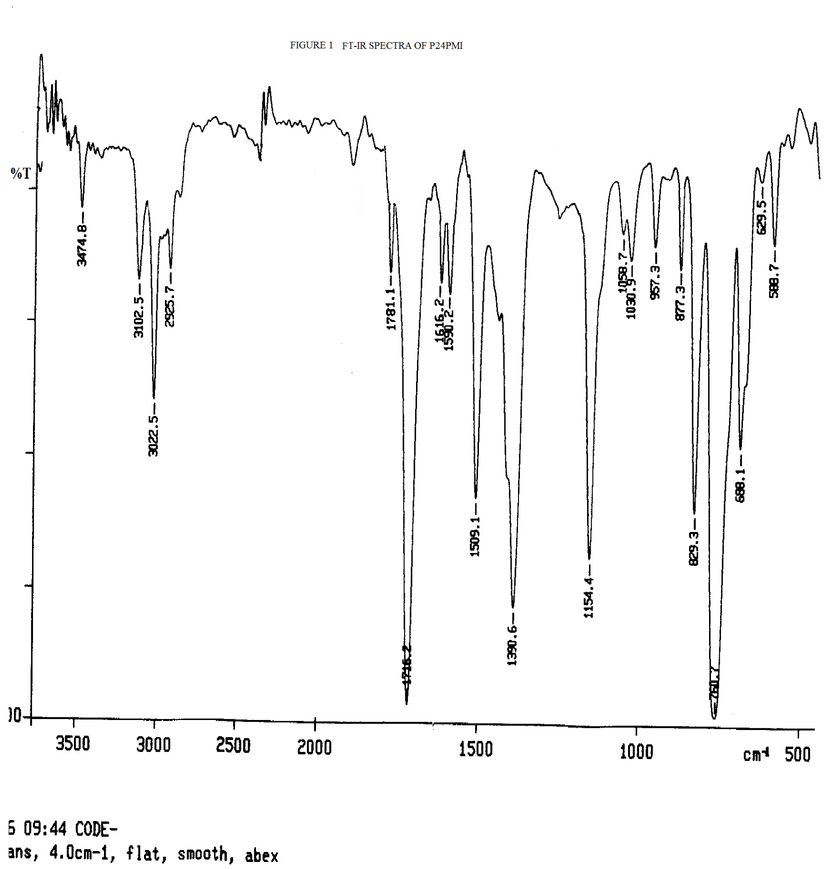


Fig. 2: FT-IR spectra of P26PMI

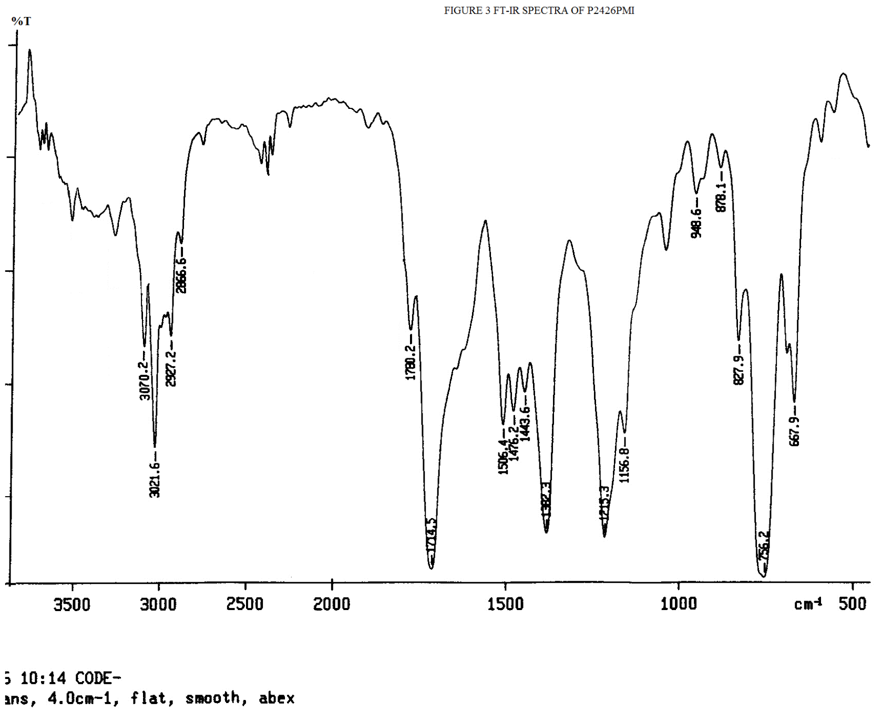


Fig. 3: FT-IR spectra of P2426PMI

^{1}H-NMR Spectral Analysis (Figure 4, 5&6)

Monomers and copolymer synthesis were also characterized by ^{1}H-NMR spectral analysis. ^{1}H-NMR spectra of samples were recorded on a Bruker DPX-300 spectrometer at 300 MH$_2$ with $CDCl_3$ as a solvent. Trimethylsilane was used as internal reference. ^{1}H-NMR spectra of the monomers and copolymer showed the following chemical shifts that have been summarized in Table 5 & 6.

Table 5: ^{1}H-NMR chemical shifts of P24PMI and P26PMI

Type of protons	P24PMI		P26PMI	
	δ Range	Multiplicity	δ Range	Multiplicity
Protons (HC=CH) of imide ring	6.85	Singlet	6.88	Singlet
Protons of phenyl ring	6.97-7.26	Singlet & Doublet	7.13-7.26	Doublet & Triplet
Protons of methyl group	2.11 & 2.35	Singlet	2.11	Singlet

Solvent peak was found at 1.5δ and 1.63δ respectively for P24PMI and P26PMI.

Table 6: ^{1}H-NMR chemical shifts of P2426PMI

Type of protons	P2426PMI	
	δ Range	Multiplicity
Protons of (CH–CH) of imide ring	3.32	Singlet
Protons of phenyl ring	7.07 – 7.42	Singlet, Doublets & triplet
Protons of methyl group	2.25,2.38,2.43	Singlet

Solvent peak was found at 1.47δ for P2426PMI.

^{1}H-NMR chemical shifts also confirm the synthesis of copolymer and their structure. These chemical shifts also confirm the copolymerization procedure. As disappearance of signal at 6.88 and 6.85 δ and appearance of signal at 3.32 δ confirm the conversion of (HC=CH) to (HC–CH) or copolymerization.

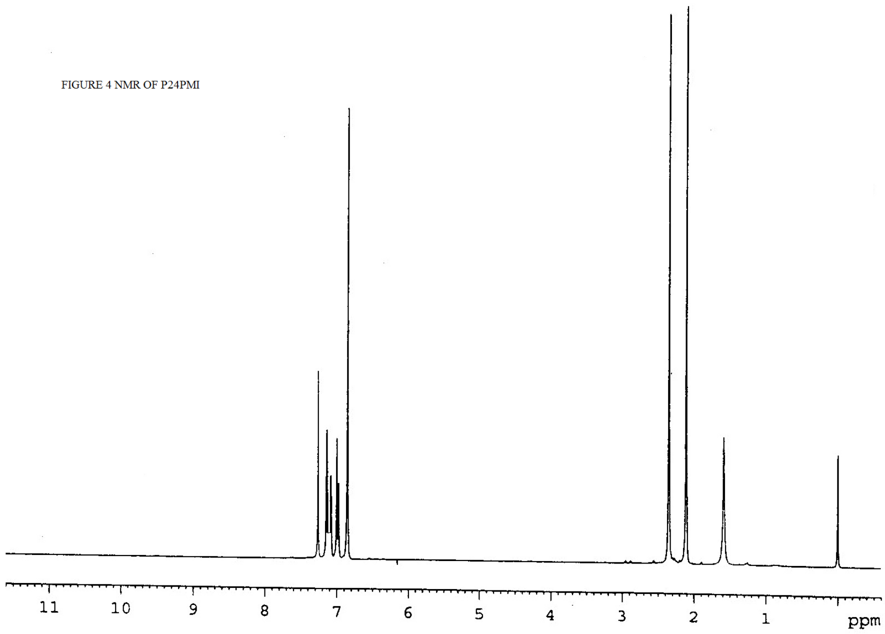


Fig. 4: NMR spectra of P24PMI

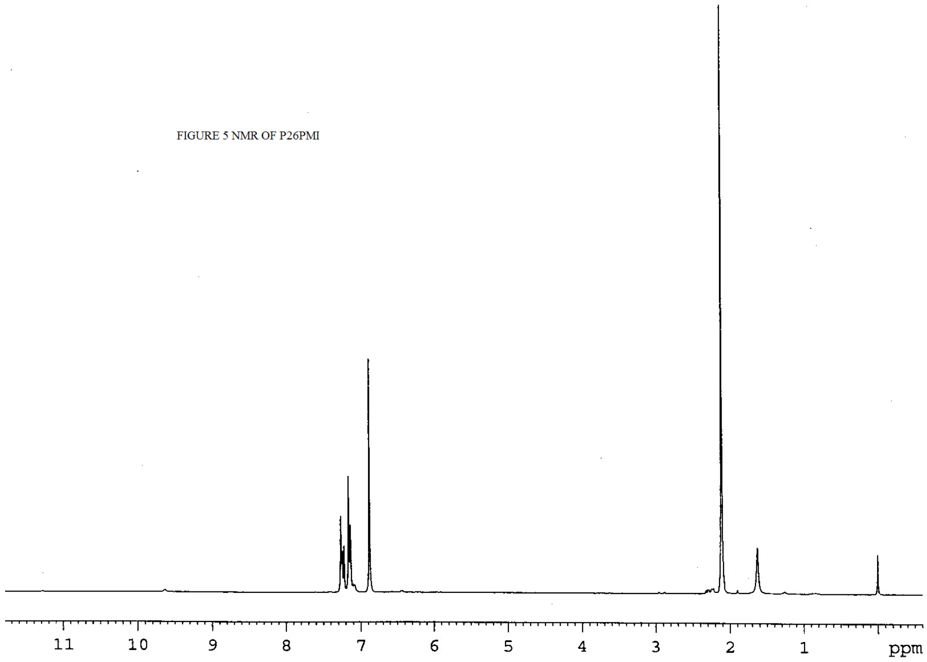


Fig. 5: NMR spectra of P26PMI

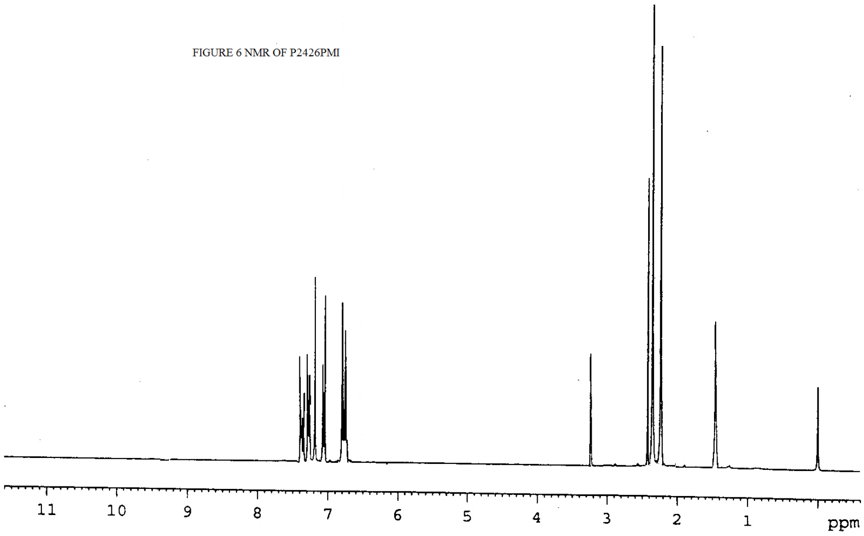


Fig. 6: NMR spectra of P2426PMI

CONCLUSION

Formation of maleimide monomers P24PMI and P26PMI was confirmed by elemental analysis, FT-IR and ^{1}H-NMR spectral analysis. C=O stretching and C=C stretching of imide ring were found to be present for P24PMI and P26PMI. Chemical shift at 6.88 δ and 6.85 δ also confirmed the synthesis of P24PMI and P26PMI respectively. Copolymerization was confirmed by presence of C–C and –C–H stretching of imide ring. 3.32 δ value also confirmed the synthesis of P2426PMI. P24PMI, P26MI and P2426PMI were completely soluble in acetone, ethanol, DMF, THF, nitrobenzene, DMSO, 1,4-dioxan and all three were completely insoluble in water.

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REFERENCES

[1] A.J. Kirbay, Polyimides – *Materials, Processing and Applications*, **1992**, 5.
[2] K.L. Mittal, Polyimides and Other High Temperature Polymer: Synthesis, Characterization, **2009**, 372.
[3] B.L. Hiran, J. Chaudhary, S.N. Paliwal, S. Meena, P.R. Chaudhary, *E-Journal of Chemistry* , **2007**, 4(2), 222.
[4] C.B. Patel, N.I. Malek, S.L. Oswal, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **2006**, 43, 289.
[5] B.L. Hiran, R. Boriwal, S. Bapna, S.N. Paliwal, *Journal of the University of Chemical Technology and Metallurgy*, **2010**, 45(2), 127.
[6] M. Biswas, New Polymerization Techniques and Synthetic Methodologies, **2001**, 7.
[7] T. Takekoshi, Polyimides, *Advance Polymer Science*, **1990**, 94, 1.
[8] B.L. Hiran, S.N. Paliwal, J. Chaudhary, S. Meena, *Journal of Indian Chemical Society*, 2007, 84, 265.
[9] M. Stevens, *Polymer Chemistry*, New York, Oxford Univ., **1999**, 96, 364.