



Trade Science Inc.

ISSN : 0974 - 7478

Volume 9 Issue 1

Macromolecules

An Indian Journal

Full Paper

MMALJ, 9(1), 2013 [18-22]

Synthesis and free radical polymerization of *N*-[4-chloro-2-methyl phenyl] maleimide and characterization of homo and copolymer

Jyoti Maheshwari¹, Dushyant Jain¹, S.N.Paliwal^{2*}, Neeru Rathore¹

¹Polymer Research Laboratory, Department of Chemistry, B.N.P.G. College, Udaipur, 313 001, Raj., (INDIA)

²Department of Chemistry, Pacific College of Engineering Udaipur, Raj., 313001, (INDIA)

E-mail: paliwalnsn_1982in@yahoo.co.in

ABSTRACT

The synthesis of *N*-[4-chloro-2-methyl phenyl] maleimide (CMPMI) was described. The homopolymer of CMPAMI and copolymer with methyl methacrylate (MMA) was synthesized by free radical copolymerization. The homo and copolymers were characterized by solubility, intrinsic viscosity, density, FT-IR and ¹H NMR spectroscopy. The thermal properties of homo and copolymer were studied by thermo gravimetric analysis (TGA).

© 2013 Trade Science Inc. - INDIA

KEYWORDS

N-[4-chloro-2-methyl phenyl] maleimide;
Methyl methacrylate (MMA);
Radical polymerization;
AIBN;
Characterization.

INTRODUCTION

Maleimide polymers have a good stability with high transition temperatures due to the polar five-membered imide ring structure. One property of substituted maleimide is their susceptibility to a variety of chemical reactions as a result of the electron withdrawing effect of the two adjacent carbonyl groups in maleimide ring, which create a very electron-deficient double bond.

Most of the aromatic polyimides have one major drawback, their intractability in fully imidized form. Furthermore there are several difficulties in processing due to insolubility^[1]. Copolymerization of maleimides with vinyl monomers provides the possibility of synthesizing higher and thermally stable polymers. In addition to that the process ability of maleimide polymer can also be enhanced by the incorporation of more flexible units within the polymer

backbone^[2]. During the past several years many reports and researches in the free radical copolymerization of *N*-substituted maleimides with various vinyl monomers have emerged^[3-9]. Maleimide based copolymers have been found to have versatile applications in many industries ranging from aerospace to the microelectronics field^[10-13]. The copolymerization process can also improve the polymer properties in order to meet specific requirements.

The present paper reports the synthesis and free radical homopolymerization and copolymerization of *N*-[4-chloro-2-methyl phenyl] maleimide with methyl methacrylate (MMA). It was observed that such polymers have better thermal stability than the polymers of vinyl monomers. The study of physical and spectral properties has been carried out in order to characterize the copolymer sample. The thermal properties of copolymer were investigated by thermo gravimetric analysis (TGA).

MATERIAL AND METHODS

Materials

4-chloro-2-methyl aniline and maleic anhydride were recrystallized from acetone. Methyl methacrylate (MMA) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor then dried over anhydrous CaCl_2 for 6 hrs and distilled^[14]. The head and tail fractions were discarded. Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol prior to use. Tetrahydrofuran (THF) was purified by distillation after being refluxed for 2 hr in the presence of sodium. *N,N*-Dimethylformamide (DMF) and methanol used for this work were of analytical grade and were used as received.

Measurements

$^1\text{H-NMR}$ spectra of monomer and polymer samples were taken in DMSO-d_6 on a Bruker DPX-200/DPX-300 spectrometer at 200/300 MHz. The internal reference used was TMS. FT-IR spectra of the monomer and polymer sample were recorded on a Shimadzu 8201 PC ($4000\text{-}400\text{ cm}^{-1}$) FT-IR spectrometer, using KBr

pellet technique. The viscosity measurements were carried out in DMF at $30\pm 0.2^\circ\text{C}$, using an Ubbelohde suspended level viscometer. The thermo grams in air were obtained on a Mettler TA-3000 system, at a heating rate of $10^\circ\text{C}/\text{min}$ from 0°C to 600°C .

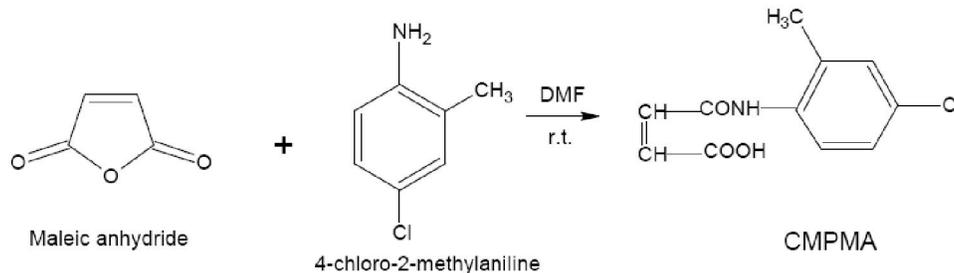
Methods

Synthesis of *N*-[4-chloro-2-methyl phenyl] maleimide (CMPMI)

CMPMI monomer was synthesized in two steps from maleic anhydride, 4-chloro-2-methyl-aniline and acetic anhydride.

Step 1: *N*-(4-chloro-2-methyl phenyl) maleamic acid (CMPMA)

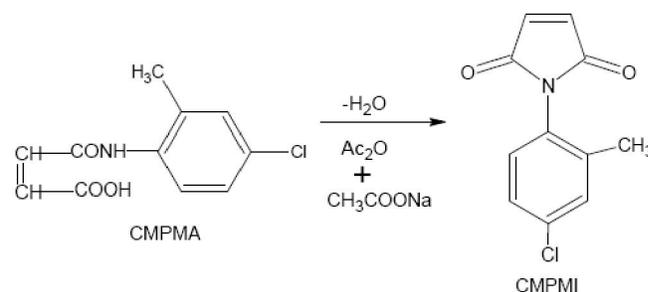
A solution of maleic anhydride (19.62g, 0.2mol) in DMF was gradually added over a period of 10 minutes to a well-stirred solution of 4-Chloro-2-methyl aniline (27.42 g, 0.2 mol) in DMF. The mixture was stirred for 2 hours at room temperature. The resulting solution was poured into a large amount of crushed ice to precipitate crude CMPMA. The crude was filtered, dried and then recrystallized from ethanol to obtain pure CMPMA in 85% yield.



Step 2: *N*-(4-chloro-2-methyl phenyl) maleimide (CMPMI)

A mixture of 23.9 g (0.1mol) CMPMA, 8.2g (0.1mol) sodium acetate and 120 ml acetic anhydride were stirred for 2 hours at $55\text{-}60^\circ\text{C}$. The reaction mixture was cooled and poured into large amount of crushed ice. The obtained light yellow mass was obtained filtered and dried at $60\text{-}70^\circ\text{C}$ and then recrystallized from methanol obtaining the product in a 75% yield with mp 231°C . The purity and structure of the monomer was ascertained by FT-IR and $^1\text{H NMR}$ spectra. FT-IR: 1777, 1718 (CONCO) 1391 (C-N) , $952, 693\text{ (CH=CH)}\text{ cm}^{-1}$. $^1\text{H NMR}$ (300 MHz, TMS, DMSO-d_6 , δ ppm) 6.95 (s, 2H, CH=CH); 7.52-7.59

(s, 1H in phenyl ring meta- to maleimido); 7.83-7.89 (d, 1H in phenyl ring meta- to maleimido); 8.10-8.26 (d, 1H in phenyl ring ortho- to maleimido); 1.3-1.6 (s, 1H, Methyl group). Above data of FT-IR and $^1\text{H NMR}$ spectral analysis confirmed the structure of APM monomer.



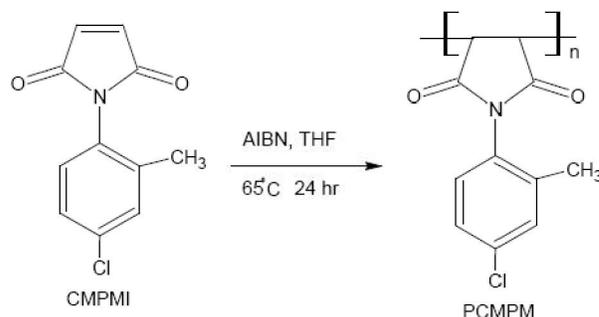
Full Paper

Homopolymerization of *CMPMI*

Radical homopolymerization of *CMPMI* (0.03 mol, 9.18 gm) were carried out using AIBN as a free radical initiator in THF. Reaction mixture was refluxed at 65°C for 24 hour. The homopolymer was isolated by precipitation in methanol containing water. The precipitated homopolymer PCMPM was washed with methanol several times and dried in a vacuum oven. A summary of polymerization conditions and physical characteristics of homopolymer are presented in TABLE 1.

Copolymerization of *CMPMI* and MMA

The copolymerization of *CMPMI* and MMA was carried in THF using 25 mg AIBN as a free radical



initiator at 65°C for 24 hours. The copolymer was precipitated in methanol-water mixture. The precipitated copolymer CCMPM was filtered and washed with methanol several times and then dried. A summary of polymerization conditions and physical characteristics of copolymer are presented in TABLE 1.

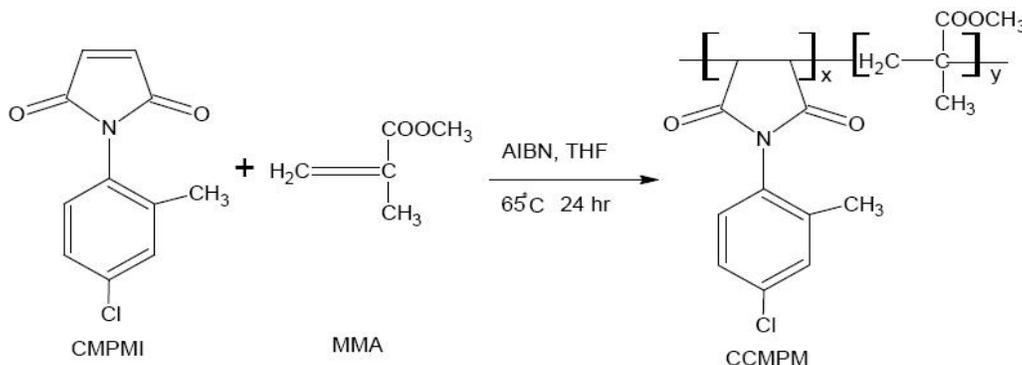


TABLE 1 : Free radical homo and copolymerization of *CMPMI* and MMA

Polymer Code	Feed mole fraction		Polymerization Time (h)	Appearance	% Nitrogen	% Yield
	<i>CMPMI</i>	MMA				
PCMPM	1.0	0.0	24	Yellow	6.21	24.1
CCMPM	0.5	0.5	24	Off White	4.23	30.2

RESULTS AND DISCUSSION

Solubility behaviour

TABLE 2 summarizes the relative solubility of homopolymer and copolymer sample in number of polar and non-polar solvents at 30°C. Solubility behaviour in the later solvents depends on the composition of polymer. The solubility of copolymer is more than homopolymer in the solvent taken. The solubility of polymer depends on composition of polymer. In homo-polymer, only maleimide unit is present in polymer back-bone. Due to rigid imide ring, homo-polymer has difficulty in solubilization in organic solvents. In copolymers containing vinyl monomer unit in back-bone is non rigid so polymer is easily soluble in different solvents.

TABLE 2 : Solubility behavior of *PCMPM* and *CCMPM* in polar and non-polar solvents at 30°C.

Solvent	<i>PCMPM</i>	<i>CCMPM</i>
Acetone	IS	S
Dioxane	IS	S
THF	S	S
DMF	S	S
DMSO	S	S
Chloroform	IS	S
Toluene	IS	IS
Benzene	IS	IS
Hexane	IS	IS
Dichloromethane	S	IS
Ethanol	IS	IS
Methanol	IS	IS
Ethyl acetate	IS	S

S=Soluble, IS=Insoluble

Physical properties

The density, intrinsic viscosity $[\eta]$ and molecular weight of the homopolymer and copolymer samples are listed in TABLE 3. The value of η depends on molecular weight as well as on the size of polymer coil in given solution. The density of CCMPM is less than water.

TABLE 3 : The Intrinsic viscosity, density and molecular weight of CCMPM

Polymer Code	ρ (g/cm ³)	η dl/g	Mw (g/mol)
PCMPM	0.8782	0.202	5689
CCMPM	0.8437	0.187	21253

Spectral characterization

The FT-IR spectrum and ¹H-NMR spectrum (300MHz in DMSO-*d*₆) of PCMPM are shown following peak and chemical shift. The absence of a sharp band at 950cm⁻¹ and chemical shift at 7.08 ppm due to CH=CH in a monomer having a vinyl group, has shifted to 3.1-3.5 ppm in the polymer^[15,16], indicates the formation of polymer via vinyl group polymerization. The presence of absorption bands at 1776 and 1714 cm⁻¹ due to asymmetric and symmetric stretching of C=O in the five member imide ring indicates that the imide ring remained intact in the polymerization.

The major characteristic absorption bands are observed at 3400- 3330 (broad, -NH stretch), 1770, 1709 (C=O asymmetric and symmetric stretch in a five member imide ring and C=O stretch of ester), 1633, 1547 (aromatic ring). These characteristic bands confirm that units of both the monomers *CMPMI* and *MMA* are present in the copolymer samples.

The ¹H NMR spectra of the copolymer showed the following chemical shifts. The δ at 8.32-7.21 ppm is of 1 Ar-H, ortho- to N of imide group while at 8.15-8.01 ppm for 1 Ar-H, meta- to N-of imide group. The δ at 7.96-7.86 ppm is for 1 Ar-H, meta- to N of the imide group. The δ observed at 3.6-3.9 ppm corresponds to overlapping of 2H -(CH-CH)_n - in the polymer main chain and 3H (-OCH₃) of *MMA* segment. The δ in the range 2.0-2.4 ppm is of 2H of methylene group while at 0.82-1.97 ppm for 3H of CH₃.

Thermal properties

It is well known that polymaleimide is a potential heat and chemical resistant material, so maleimide is

widely used as a co-monomer for modified polymeric systems. Only single step degradation at temperature of over 300°C was observed for polymaleimide in TGA. The thermo grams were obtained by heating polymers in air at 10°C/min. The results of percentage weight loss suffered from 100°C to 500°C at 100 intervals are summarized in TABLE 5.

The initial decomposition temperature *T_i*, temperature for maximum weight loss *T_{max}*, and final decomposition temperature *T_f* of first and second degradation steps are given in TABLE 4.

TABLE 4 : Thermal behaviour of polymers

Polymer	<i>T_i</i>	<i>T_{Max}</i>	<i>T_f</i>	Residue at 500° C
PCMPM	270	350	390	10%
	390	450	590	
CCMPM	230	310	360	5%
	360	400	530	

TABLE 5 : Percentage weight loss of CCMPM at various temperatures from the TGA.

Polymer	Weight loss (%)			
	200°C	300°C	400°C	500°C
PCMPM	0.5	8	70	90
CCMPM	1	10	74	95

TABLE 4 reveals that all homo and copolymers shows two steps degradation and homopolymer shows better stability than copolymers. The first decomposition step occurred around 350°C, which may corresponds to the decomposition of phenyl and aliphatic alkyl ester segment of *MMA* in copolymer. The second step is degrading around 360°C, which may correspond to the rigid imide segment of maleimide unit in polymer. It's indicating that thermal stability tends increase as the maleimide content is increased.

The results of percentage weight loss suffered from 100°C to 600°C at 100 intervals are furnished in TABLE 5. The weight loss decreases with an increasing of *CMPMI* content in polymers. TABLE 5 also reveals that weight loss was below to 0.5-8% up to 300°C in homo polymer and 0.5 -10% up to 200°C in both copolymer samples.

CONCLUSION

Free radical copolymerization of *CMPMI* with

Full Paper

MMA has produced a random copolymer. The investigate copolymaleimides shows better physical properties like intrinsic viscosity and molecular weight than homopolymaleimide. The copolymer show excellent solubility in THF, DMF, DMSO, Dioxane and cyclohexanone. The thermal behaviour of homopolymer is better than copolymer and other properties like as intrinsic viscosity, molecular weight, solubility of copolymers is better than homopolymer.

ACKNOWLEDGEMENT

We are thankful to CDRI Lucknow and SICART Vallabh-vidhyanager for analysis work. The authors wish to thank Dr. B.L.Hiran, Retired Professor, Department of Chemistry, M.L. Sukhadia University, Udaipur (Raj) for his constant encouragement and guidance.

REFERENCES

- [1] T.Pyriadi, M.Hamad; *Polymer*, **37**(23), 5283 (1996).
- [2] I.K.Verma, A.K.Gupta, D.S.Varma; *Addition Polyimides, International Journal of Applied Polymer Science*, **28**, 191 (1983).
- [3] H.M.Li, S.A.Lin; *Journal of Macromolecular Science Pure and Applied Chemistry*, **A37**(11), 1475 (2000).
- [4] L.Y.Grishchuk, L.A.Vretik, V.G.Syromyatnikoy; *Vysoko Molekulyarnye Soedineniya Ser.A*, **49**(2), 238 (2007).
- [5] B.A.Howell, J.Zhang; *Journal of Thermal Analysis and Calorimetry*, **83**(1), 262 (2006).
- [6] H.Wang, J.Wei, X.Jiang, J.Yin; *Polymer International*, **55**(8), 930 (2006).
- [7] K.H.Park, J.T.Lim, S.Song, M.G.Kwak, C.J.Lee, N.Kim; *Reactive and Functional Polymers*, **40**(2), 169 (1999).
- [8] C.Gaina, V.Gaina; *Designed Monomer and Polymers*, **7**(3), 235 (2004).
- [9] E.Bezdushna, H.Ritter; *Macromolecular Rapid Communications*, **26**(13), 1087 (2005).
- [10] L.Takao, N.Tsutomu, F.Wakichi, T.Masao; *Journal of Applied Polymer Science*, **60**, 36 (1996).
- [11] J.Y.Chang, T.J.Kim, M.J.Han; *Polymer*, **38**(18), 4651 (1997).
- [12] N.C.Sharma, S.Husain; *Journal of Indian Chemical Society*, **74**, 781 (1997).
- [13] B.L.Hiran, J.Chaudhary, S.N.Paliwal, S.Meena; *Journal of Indian Chemical Society*, **84**, 385 (2007).
- [14] J.A.Riddick, W.B.Bunger, T.K.Sakano; *Organic Solvents; Physical Properties and Methods of Purification*, Willey Inter Science, New York, (1986).
- [15] R.K.Sadhir, J.D.B.Smith; *Journal of Polymer Science: Polymer Chemistry*, **30**, 589 (1992).
- [16] L.Chunqing, L.Huaming, L.Pengsheng; *Journal of Macromolecular Science Part A: Pure and Applied Chemistry*, **41**(10), 1161 (2004).