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Studies on Thermal and Microbial Resist PolyN-[(4-Chloro, 2-(Phenylcarbonyl) phenyl] maleimide: Synthesis and characterization

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Abstract:

N-[(4-chloro, 2-(phenyl carbonyl)phenyl]maleimide (CPMI) was homopolymerized and copolymerized with methyl /ethyl/butyl acrylates (MA/EA/BA) at 60-70^{0}C in tetrahydrofuran (THF) solution with azoisobutyronitrile (AIBN) as an initiator. The structure of monomer, homopolymer and copolymers were elucidated by FT-IR, ^{1}H-NMR and elemental analysis. The nine copolymer samples were synthesized from different feed ratio of comonomers. The monomer reactivity ratio were determined by Finemann Ross method. The investigated homo and copolymers showed solubility in polar solvents. Thermal behavior of homopolymer and copolymers were evaluated by TGA. The molecular weights were determined by GPC. The antimicrobial activity of synthesized homopolymer and copolymer were screen and they showed excellent antimicrobial activity.

Keywords: THF, reactivity ratio, TGA, Finemann-ross method, antimicrobial activity.

Introduction

N substituted phenyl maleimides are a type of heat resistant monomer, which have a planar five member ring. The presence of imide ring in backbone provide polymers with superior mechanical and thermal stability to the polymer [1]. They possess unique properties of chemicals and electrical resistance, good adhesion and cohesion to different kind of materials and heat resistance[2]. The heat resistance can be improved, if it embedded in the polymer chain because the imide ring increase the internal rotation resistance of the chain. Not only the heat resistance can be improved but also process ability, hot melting and abrasion resistance property will be enhanced[3]. N-substituted phenyl maleimide is a type of heat resistant monomer which have many excellent properties such as high flexibility and hydrophobicity, low surface tension, low glass transition temperature (Tg), weather resistance, and excellent thermal stability, but the low tensile strength and relatively high costs limit their applications. Copolymerization techniques have a number of advantages in controlling the degree of functional groups in the product, controlling its structure, and predicting the distribution of groups within the copolymer[4]. The reactive double bond in maleimide is an electron - deficient group, which makes it easy for maleimide to form alternating copolymers with electron- rich monomers[5]. The copolymers of maleimide usually have a relatively high glass transition temperature (Tg) and thermal decomposition temperature since the polymer chain are hindered by the rigid five member ring[6] Acrylates based polymers have many specific features such as good film-forming, gloss, transparency, and mechanical properties, and their corresponding products have been widely used as coating, paints, and adhesives. Thus, the combination of acrylates and maleimide has been of importance and interest during the past few years. The antimicrobial property of the polymer plays an important role for many of its application. Contamination by microorganism is of great concern in several areas such as medical devices, health care products, water purification systems, hospital and dental equipment, etc. One possible way to avoid the microbial contamination is to develop materials possessing antimicrobial activities [7]. In this work we focus on the attempt to produce copolymers with better thermal stability than the polymers of vinyl monomer. The physical spectral and thermal properties have been studied in order to characterize the coploymers.

Materials and Method

Azobisisobutyronitrile (AIBN), Methyl acrylate (MA), Ethyl acrylate (EA), Butyl acrylate (BA), THF, DMF was purchasedfrom Lobachemicals. All other reagents were used of analytical grade commercial products and used without any Additional purification.

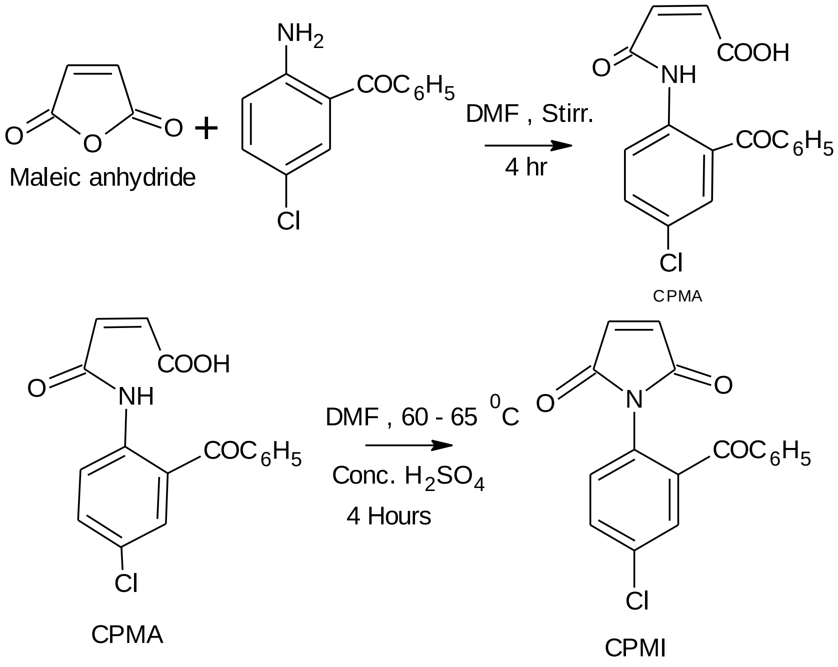
Synthesis of Monomer

The monomer N-[4-Chloro-2-(phenyl carbonyl) pheny]maleimide **(CPMI) [Scheme 1]** was obtained by the reaction of maleic anhydride with 2-amino, 5-chlorobenzophenone according to a reported method [8]. The monomer **CPMI** was homopolymerized and copolymerizedwith Methyl/Ethyl/Butyl acrylate (MA/EA/BA) **[Scheme 2].**

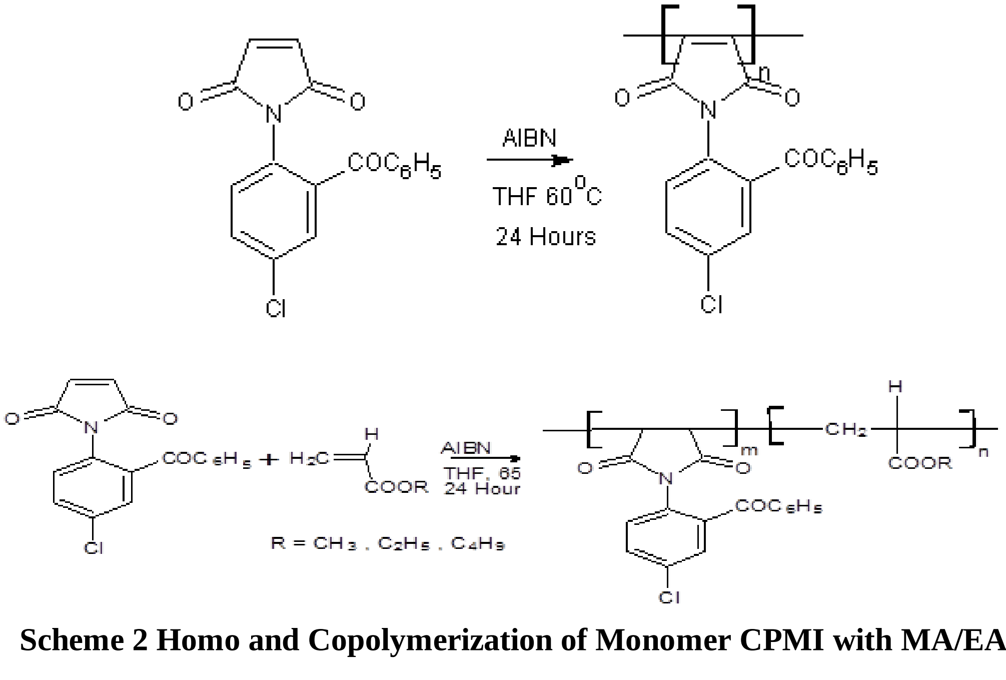
Result and Discussions

Characterization

Fourier transform infrared (FTIR) spectra was recorded on a FTIR Perkin-Elmer spectrophotometer model RX-I. The sample was prepared in KBr pellets, and the spectrum was obtained in the range 250-4000 cm−1. Nuclear Magnetic Resonance (NMR) spectra of newly synthesized monomer, homopolymer and copolymer have been scanned on BRUKER AVANCE II 400 MHz NMR Spectrometer. TMS use as a reference.



Scheme 1: Synthesis of Monomer CPMI



Scheme 2 Homo and Copolymerization of Monomer CPMI with MA/EA/BA

Structure of Monomer **[CPMI]**, Homopolymer **[H-CPMI]** and Copolymer **[C-CPMI]** were evaluated by FT-IR and ^{1}H-NMR spectroscopy. **[Table 1]** show the IR and ^{1}H-NMR spectrum of the new resulting homopolymer and copolymers. In homopolymer and copolymer peak at 1584 cm$^-$, 948 cm$^-$ and chemical shift at 6. 9 - 7. 14 (s) ppm due to C-C stretch of CH=CH, C-H bending of CH=CH was disappear. The disappearance of this peak in polymer H-CBMI C-CBMI shows that the radical polymerizations proceed through opening of the double bond. From the IR spectral studies, it has been revealed that all three copolymers give rise to nearly similar spectral patterns..

Table 1FT-IR and ^{1}H-NMR spectral data of CPMI, H-CPMI and C-CPMI

Techniques	CPMI	H-CPMI	C-CPMI	Characteristics
FT-IR (cm$^-$)	1719	1756	1719	C=O Sym. &Asym. stretch of imide
	1359	1368	1378	C-N-C stretch of N - Substituted maleimide
	3031	3031	3028	C-H stretch of aromatic CH=CH
	948	**-**	**-**	**C-H bending CH=CH**
	1584	**-**	**-**	**C-C stretch in CH=CH**
	-	-	2958, 2925	C-H stretch in CH_3, CH_2 (MA)
	-	-	2956, 2926	C-H stretch in CH_3, CH_2 (EA)
	-	-	2960, 2933	C-H stretch in CH_3, CH_2 (BA)
	-	-	1184	C-O-C stretch of ester
^{1}H-NMR (ppm)	6. 92	6. 6	6. 6	Phenyl proton of Ortho to N of imide
	7. 56	7. 52	7. 6	Phenyl proton of Meta to N of imide
	6. 6	**-**	**-**	**(CH=CH)**
	-	**3. 40**	**3. 54**	**$-[CH-CH]_n-$**
	-	-	2. 1	$-CH_2-$
	-	-	0. 9-1. 6	Methyl of acrylate
	-	-	3. 8	$-OCH_3$

Physical Properties

Homo and Copolymers were soluble in polar solvents like THF, DMF, DMSO, Acetone, 1, 4 – Dioxane, and dichoromethane and partially soluble in nonpolar solvents like N – hexane, Toluene, Benzene.

Density (ρ) depends on packing of Molecules in polymer chains. The density of homopolymer and Copolymer were determined at 30 ^{0}C, by using Density bottle. Density of Homopolymer and Copolymer are given in **[Table 2]**.

The intrinsic viscosity of synthesized homopolymer and copolymers have been evaluated using Ubbelhode Suspended Level Viscometer at different concentrations ranging from 1. 00 to 0. 1% of copolymer in DMF at 30 ^{0}C. Intrinsic viscosity [η] were calculated from plots of $\eta_{red.}$ against Concentration. By extrapolating linear plot to zero concentration, intercepts on the viscosity function axis give [η] value in plots. It was observed that copolymer having higher (Mn) showed higher value of [η] **[Table 2].**

GPC data of synthesized polymer were given in **[Table 2]**. It showed that as the alkyl group increases in the copolymer, the molecular weights of polymers decreases, which may be due to relative bulky groups in co-monomer. Polydispersity indices ranging from 1. 2 to 2. 0 clearly suggested that the mechanisms for the formation of homo and copolymer proceed through free radical polymerization.

Copolymer Composition

The copolymer compositions of samples were determined by N% analysis, since CPMI monomer (M_1)contains nitrogen while Acrylates monomer does not have any nitrogen. Thus, the N% in the copolymers can safely be used to estimate the copolymer composition. The monomer reactivity ratios were calculated using Fineman-Ross method[9]. The values of r_1= 0. 149 and r_2= 0. 1289 In our case, the monomer CPMI is also more active. Effective reactivity ratios for CPMI (M_1) and BA (M_2) are given in **[Table 4]**. The reactivity ratios r_1 and $r_2$are the slope of FR plot and its intercept. The Q and e values were calculated using the Alfrey-Price equation [10]. Alfrey- Price used empirical parameters Q and e to represent the resonance stability of monomer M_1 and polarity of the radical M_1*. The values of Q and e are shown in **[Table 4]**.

Table 2: Intrinsic viscosity, Density, Molecular weight of Homopolymer(H-CPMI) and Copolymer(C-CPMI)

Polymer Code	Density (gm/cm)	Viscosity (η) (gm/dl)	Molecular weight (Mn)	Molecular weight (M_w)	PDI (Poly Dispersity Index)
H-CPMI	0. 598	0. 071	4078	5056. 8	1. 239
C-CPMI-MA	0. 786	0. 103	3067	6245	2. 036
C-CPMI-EA	1. 256	0. 115	4568	7382	1. 616
C-CPMI-BA	1. 884	0. 121	5089	8345. 7	1. 6399

Table 3 Parameters for Fineman-Ross Methods to Determine Reactivity Ratios in Copolymer ofC-CPMI-BA

Code	Mole Ratio Feed		W% of C-CPMI-BA	Mole Fraction of C-CPMI-BA		Finemann –Ross Method	
	x_1: x_2	% N		Feed X_1	Copolymer F_1	X1(1-2F1) / (1 - X1)F1	X_1^2(F1-1)/ $(1-X1)^2$F1
C-CBMI-BA-1	1: 9	2. 46	39. 54	0. 1	. 127	0. 6491	-0. 084
C-CBMI-BA-2	2: 8	2. 95	47. 42	0. 2	. 152	1. 1481	-0. 340
C-CBMI-BA-3	3: 7	3. 23	51. 92	0. 3	. 266	0. 7526	-0. 501
C-CBMI-BA-4	4: 6	3. 52	56. 59	0. 4	. 381	0. 4166	-0. 722
C-CBMI-BA-5	5: 5	3. 88	62. 37	0. 5	. 421	0. 3761	-1. 371
C-CBMI-BA-6	6: 4	3. 99	64. 14	0. 6	. 496	0. 0202	-2. 291
C-CBMI-BA-7	7: 3	4. 04	64. 95	0. 7	. 518	-. 1612	-5. 130
C-CBMI-BA-8	8: 2	4. 30	69. 13	0. 8	. 622	-1. 5725	-10. 041
C-CBMI-BA-9	9: 1	5. 71	91. 80	0. 9	. 756	-6. 7215	-23. 714

Table 4 Reactivity ratios of Monomers

Polymer Code	Reactivity Ratios (Finemann-Ross Method)		Alfrey and Price Method	
	r_1	**r_2**	**Q**	**E**
C-CBMI-BA	0. 149	0. 1289	0. 56	3. 04

Effect of Solvent – Initiator

The percentage yield of homo and copolymers were determined in different solvents and initiator. It was observed that percentage yield in THF-AIBN system is high as compared to DMF, Acetone, Dioxane solvents. Due to high viscosity of THF than the other solvents. Viscosity of solvents are high, life of free radicals and polymerization will be high. Viscosity of DMF is less than the other solvents, thus percentage yield was less **[Table 5].**

Table 5 Effect of Solvents and initiators on percentage yield of Polymer

Solvents	Solvent Viscosity	Polymerization Time	% Yield in AIBN initiators H-CPMI	% Yield in BPO initiators H-CPMI	% Yield in AIBN initiators C-CPMI-BA	% Yield in BPO initiators C-CPMI-BA
DMF	1. 299	18 h	28. 34	24. 73	26. 15	29. 15
Acetone	1. 359	18 h	29. 08	25. 18	30. 42	31. 55
Dioxane	1. 416	18 h	34. 45	29. 65	36. 72	42. 22
THF	1. 497	18 h	42. 12	38. 27	40. 13	44. 14

Thermal analysis

The thermal stability of the homo and copolymers were ascertained usingthermogravimetric analysis (TGA)over a temperature range from room temperature to 800℃ under air atmosphere at heating rate of 10℃ min-1. TGA curves are shown in and corresponding decomposition data are listed in[**Table 6]**. TGA thermograms of the homopolymer and copolymers decompose by two-step degradation mechanism at temperature of over 210^0C. The TGA results are summarized in [**Table 6, 7]**. The thermal stability increases on increasing the content of maleimide derivatives in the copolymers, which is due to the good thermal stability of maleimide polymers attributed to the polar five-member imide ring structure.

Antibacterial activity

Antibacterial activity of monomer, homopolymer and copolymer of CPMI with MA, EA & BA were studied against gram positive and gram negative bacteria and plant pathogenic organism at a 100 (μg/ml) by Agar cup well method. The THF solvent was used as control in this method. It has been observed that the presence of chlorine content in CPMI and acrylate and chlorine in homopolymer and copolymer showed antibacterial activity. The antibacterial activity of monomer and copolymer against bacteria are shown in following **[Table 8, 9].** CPMI and H-CPMI, C-CPMI-MA, C-CPMI-EA, C-CPMI-BA screens their antibacterial activity against bacteria (***Esherichia Coli, Peudomonasaeruginosa***) and antifungal activity against fungus ***(Aspergillusnizer. Alternariasolani)***

Table 6: Thermal behavior of Homopolymer and Copolymer

Polymer Code	Ti	Tmax	Tf	Residue at 500^0C
H-CPMI	215	230	310	25. 33
	440	525	560	
C-CPMI-BA	210	265	325	22. 83
	330	370	420	

Table 7: Percentage weight loss of Homopolymer and Copolymer at various temperatures from the TGA

Polymer	200^0C	300^0C	400^0C	500^0C	600^0C
	Weight loss (%)				
H-CBMI	13. 89	44. 12	54. 58	74. 67	94. 80
C-CBMI-BA	10. 91	48. 98	56. 43	77. 17	97. 17

Table 8: Antibacterial activity of CPMI, H-CPMI, C-CPMI-MA, C-CPMI-EA, C-CBMI-BA against bacteria *E. Coli, P. aeruginosa*

Code	500(µg/ml) Concentration of compound taken	
	Zone of Inhibition For E. coli (mm)	**Zone of inhibition for P. aeruginosa (mm)**
CPMI	9	8
H-CPMI	12	12
C-CPMI-MA	13	12
C-CPMI-EA	15	15
C-CPMI-BA	18	7

Table 9 Antifungal activity of CPMI, H-CPMI, C-CPMI-MA, C-CPMI-EA, C-CPMI-BA against fungus *A. nizer, A. solani*

Code	**100(µg/ml) Concentration of compound taken**	
	Zone of Inhibition For A. nizer (mm)	**Zone of Inhibition For A. solani (mm)**
CPMI	**7**	**9**
H-CPMI	**10**	**8**
C-CPMI-MA	**12**	**14**
C-CPMI-EA	**15**	**11**
C-CPMI-BA	**20**	**18**

CONCLUSION

The free radical homo and copolymerization of CPMI have been carried in THF solvent. The Homo and Copolymers were characterized by elemental analysis, FT-IR, ^{1}H-NMR, spectral analysis. The synthesized homo and copolymers showed good thermal stability and degraded in two step due to side group elimination. The total heat of combination of the homo and copolymers changes linearly. The change in peak value of heat release rate and char yield depends on the chemical structures of the polymers. The biological activities of the monomer and polymers were also investigated in this study. These copolymers could be promising materials for antimicrobial coating application.

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