Copolymers of N-Substituted Maleimide with Acrylamide [AM]/ 2-Hydroxy ethylmethacrylate [OHEMA]:- Synthesis, Characterization and Thermal Behaviour

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Abstract

This article describes the synthesis and characterization of copolymers of N-(4-acetylphenyl)maleimide (APMI) with Acrylamide [AM] and 2-hydroxy ethylmethacrylate (OHEMA) were prepared by free radical polymerization. The synthesized copolymers was characterized by viscosity measurement, density measurement. FT - IR and ^{1}H- NMR spectroscopic methods. The nine copolymer samples were synthesized from different feed ratio of comonomers. The monomer reactivity ratio r_{APMI}, r_{AM} and r_{OHEMA} are determined by Finemann Ross method. Thermal behavior of copolymers was evaluated by TGA and DSC. The investigated copolymers degrade in one step. The molecular weight was determined by GPC.

Keyword: Copolymerization, Acrylamide, Reactivity ratio, TGA, GPC.

INTRODUCTION

The polymer with heat resistance and good mechanical properties are the requirements of present day technology. Among the thermally stable polymers with good mechanical properties, polyimides possess such properties[1]. Polyimides are belongs to a class of high performance polymers.

Copolymerization is one of the important techniques for systematic changes in the properties of the polymers. Copolymers with reactive or functional monomers are steadily gaining importance. Many copolymers with reactive functional groups are

now being synthesized, tested and used not only for their macromolecular properties[2-3].

Herein, we discuss on the synthesis and characterization of copolymers containing acrylate-maleimide units as electron rich and electron acceptors units with the results of their thermal and antimicrobial properties. It was observed that such copolymers have better thermal stability than the polymers of vinyl monomers. The physical, spectral and thermal properties have been studied in order to characterize the homo and copolymer.

## EXPERIMENTAL

Materials and Method

All chemicals were used as received. 4-Amino acetophenone, Maleic anhydride, Acrylamide (AM), 2-Hydroxy ethylmethacrylate (OHEMA), THF, AIBN were purchased from Sigma Aldrich.

Copolymer APMI-co-AM and APMI-co-OHEMA was synthesized according to reported method[4] **[Scheme 1].** Structure was confirmed by FT-IR and ^{1}H-NMR.

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 used as a reference. FT-IR and ^{1}H-NMR data are summarized in Table 1 and 2.
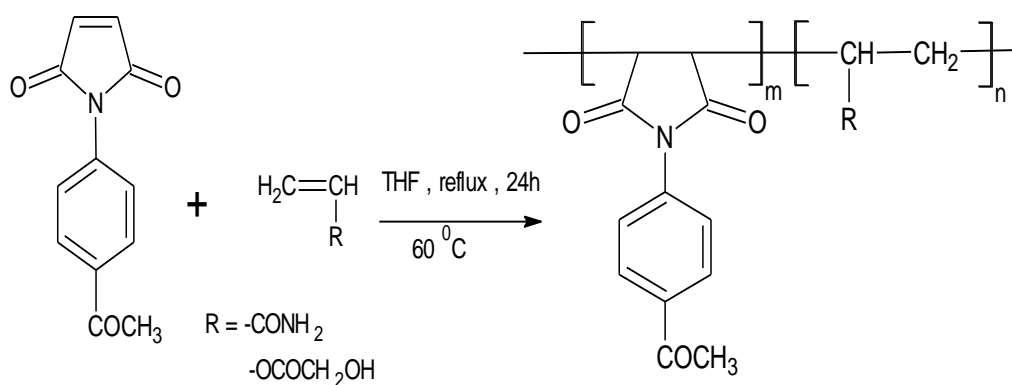
Scheme 1 Synthesis of Copolymers

Molecular weight

The molecular weight of the synthesized copolymers was measure by Gel permeation chromatography (GPC) analysis. GPC is a reliable and fast technique to determine the polydispersity index (PDI) and molar mass averages of polymers. The number average and weight average molecular weights (Mn, Mw) and polydispersity index of epoxy resin were summarizes in **[Table 3]**.

Table 1: FT-IR data of Copolymers

Characteristics	Peaks (cm^{-1})	
	APMI-co-AM	**APMI-co-OHEMA**
C=O sym. & asym. stretching in imide ring	1770,1714	1770,1714
C-N-C stretching in imide ring	1403	1403
C-H stretching of aromatic CH=CH bond	3037	3037
N-H stretching	3270	-
C-H stretching in CH$_3$, CH$_2$	2978,2929	2980,2928
C-O-C stretching of ester	-	1182
C-H bending in cis CH=CH	**Disappeared***	**Disappeared***
C-C stretching in CH=CH	**Disappeared***	**Disappeared***

Table 2: ^{1}H-NMR data of Copolymers

Type of Proton	Signal (ppm)	
	APMI-co-AM	**APMI-co-OHEMA**
Phenyl proton of ortho to N of imide	7.7	7.8
Phenyl proton of meta to N of imide	8.0	7.9
Methyl proton (-CH$_3$)	2.6	2.6
Proton of –CONH	10.6	-
Methanediyl proton (-CH$_2$-)	1.2	1.3
Proton of –OH	-	5.1
Methylene proton (CH=CH)	**Disappeared***	**Disappeared***
-[CH-CH]$_n$-	**3.3**	**3.8**

*Peaks are disappeared due to polymerization

Copolymer Composition and Reactivity Ratios

The molar percentages of the comonomer units (m_1 and m_2) in APMI-co-AM and APMI-co-OHEMA were calculated with elemental analysis data (content of nitrogen). To determine the monomer reactivity ratios, the copolymerization of APMI with AM and OHEMA using various monomer feed ratios by application of Fineman-Ross (FR) method[5]. The reactivity ratios r_1 and r_2 is the slope of FR plot and its intercept on y-axis, respectively.

Alfrey and price derived a relationship to compute the reactivity ratios of various monomers. This method deals with the resonance stabilization (Q) and polarization characteristics (e) of a monomers and its reactivity behavior with reference to another monomer radical[6]. **[Table 4]** The value of r_1 is less than r_2 in both polymers indicates reactivity of other comonomer is higher than the maleimide monomer, maleimide monomers is less reactive. Values of r_1 and r_2 indicate distribution of monomer in polymer chain is random distribution of polymer. Reactivity of Acrylamide (AM) is high in comparison to 2-Hydroxy ethylmethylacrylate (2-OHEMA), It shows that in copolymerization with maleimide moiety reactivity of vinyl pyridine is high. The value of Q and e by Alfrey-Price equation are summarized in Table 4. Large values of e indicate the electron acceptor nature of maleimide monomer.

Table 3: Density, Viscosity, Molecular Weight and PDI value of copolymers

Polymers	Density	Viscosity	Mn	Mw	PDI(Mw/Mn)
APMI-co-AM	0.562	0.390	165.8	357.9	2.158
APMI-co-OHEMA	1.38	0.073	167.6	312.6	1.865

TGA Analysis

Data derived from TG curves are furnished in **[Table 5]** Thermogram of copolymers is given in Figure 1, depicts one step decomposition reaction. Examination of TGA data reveals that the copolymers start degradation around 100 ^{0}C and remain **38.59**% of APMI-co-AM and 33.046 % of APMI-co-OHEMA around 700 ^{0}C.

Thermal stability of APMI-co-AM is higher than APMI-co-OHEMA, because Here thermal stability depends on electron substituent effect and size of group present on vinyl monomer.

Table 4. Reactivity ratios of Monomers

Polymer Code	Reactivity Ratios(Finemann-Ross Method)		Alfrey and Price Method	
	r_1	r_2	Q	e
APMI-co-AM	0.6034	0.8912	0.32	1.01
APMI-co-OHEMA	0.1151	0.2173	0.96	1.78

Table 5. TGA Analysis of copolymers

Polymer code	200 ^{0}C	300 ^{0}C	400 ^{0}C	500 ^{0}C	600 ^{0}C	700 ^{0}C
APMI-co-AM	11.235	26.198	32.518	51.868	54.329	61.419
APMI-co-OHEMA	10.311	30.182	36.515	48.355	59.436	66.954
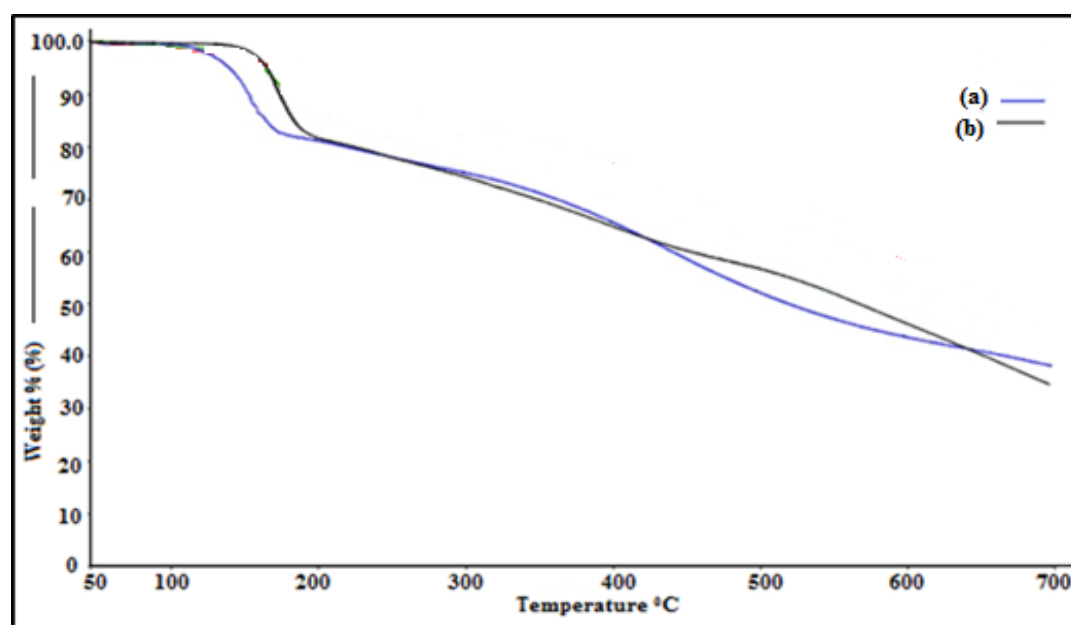
Fig. 1. TGA Analysis curve

CONCLUSION

The Radical copolymerization of APMI was carried out in THF solvents using AIBN as a initiator. The structure of synthesized copolymers was confirmed by FT-IR and ^{1}H-NMR spectral analysis. The molecular weight of homopolymer and copolymer were determined by GPC. The synthesized homopolymer and copolymer was degrade in two steps and shows excellent thermal stability up to 700 ^{0}C. The copolymers

derived from APMI with AM and OHEMA with different ratios show that the reactivity ratio of APMI, r_1 is less than r_2. This result shows higher reactivity of AM and OHEMA as compared to APMI. Copolymer showed better thermal stability.

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