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SYNTHESIS AND FREE RADICAL POLYMERIZATION OF N-[4-FLUORO PHENYL] MALEIMIDE AND STUDY OF PROPERTIES OF POLYMERS

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ABSTRACT

Free radical copolymerization of N-[4-fluoro phenyl] maleimide (PFPM) with MMA was investigated. The free radical copolymerization was carried out in THF using AIBN as an initiator at 60°C. This copolymer has better thermal stability than the polymers of vinyl monomers. The investigated copolymer show excellent solubility in THF, DMF, DMSO, dioxane, chloroform, and ethyl acetate. The copolymer is good thermal stable and degraded in two steps. The copolymers were characterized by solubility, intrinsic viscosity, FT-IR and ^{1}HNMR spectroscopy. The thermal properties of copolymer were studied by TGA.

Keywords: N-[4-fluoro phenyl] maleimide, Methyl methacrylate, THF, Free radical polymerization.

INTRODUCTION

The development of processable high-performance polymers with increased thermal stability, heat resistance and good mechanical properties has become an important problem[1]. Aromatic polyimides are one of the most important classes of high-performance polymers. Due to their thermal, electrical and high-temperature mechanical properties, aromatic polyimides have found many applications as high temperature insulators, coatings, adhesives and matrices for high-performance composites[2-6]. N-phenyl maleimide monomers with halogen substituent in the aromatic ring have been studied only in a few cases [7]. Anionic polymerization is a good method to obtain homopolymer[8-10]. The present paper reports the synthesis and free radical copolymerization of N-[4-fluoro phenyl] maleimide, with methyl methacrylate (MMA). This copolymer has better thermal stability. Copolymer composition is determined by elemental analysis and thermal study was done with the help of TGA analysis.

EXPERIMENTAL

Materials

4-fluoro aniline was purified by vacuum distillation and maleic anhydride was 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 8 h and distilled. The head and tail fractions were discarded. AIBN (2, 2'-azobis–isobutironitrile) was recrystallized from methanol prior to use. THF, DMF and Methanol used for this work were purified by distillation. Other reagent and solvent were of analytical grade.

Methods

Synthesis of monomer N-[(4-fluoro phenyl) maleimide (PFPM)

N-[(4-fluoro phenyl) maleimide was synthesized in two step using 4-fluro aniline and Maleic andhydride.

Preparation of N-(4-fluoro phenyl) maleamic acid

4-fluoro aniline (11.1 gm, 0.1 mole) and maleic anhydride (9.8 gm, 0.1 mole) were taken in 30 ml DMF solvent. This reaction mixture was stirred for three hours at room temperature (25-30ºC). After three hours stirring this solution was added to crush ice water. The white solid N-(4-fluoro phenyl) maleamic acid was filtered and dried. It was crystallized by ethanol to obtained pure N-(4-fluoro phenyl) maleamic acid.

Cyclodehydration of the N-(4-fluoro phenyl) maleamic acid

This intermediate N-(4-fluoro phenyl) maleamic acid was cyclodehydrated by treating with acetic anhydride and sodium acetate. This solution N-(4-fluoro phenyl) maleimic acid in acetic anhydride was stirred for three hours at 80ºC. Solution poured into crushed ice to obtained white solid precipitate followed by filtration and washed with water and $NaHCO_3$ solution. Obtained product N-[(4-fluoro phenyl) maleimide] was crystallized by ethanol.

Homopolymerization of N-(4-fluoro phenyl) maleimide or preparation of (HPFPM)

Homopolymerization of N-(4-fluoro phenyl) maleimide was carried out in THF solvent by using AIBN, as free radical initiator AIBN, at 60 ºC. N-(4-fluoro phenyl) maleimide (19.1 gm, 0.01 mole) and THF 200 ml were refluxed in round bottom flask with reflux condenser. To this solution 50 mg AIBN was added and the reaction mixture was refluxed on heating mental at 60 ºC for 24 hours. Equal amount methanol and water mixture was used to precipitate the homopolymer. The crude product was dissolved in THF and reprecipitated in methanol this process was repeated twice to completely remove the unreacted monomer.

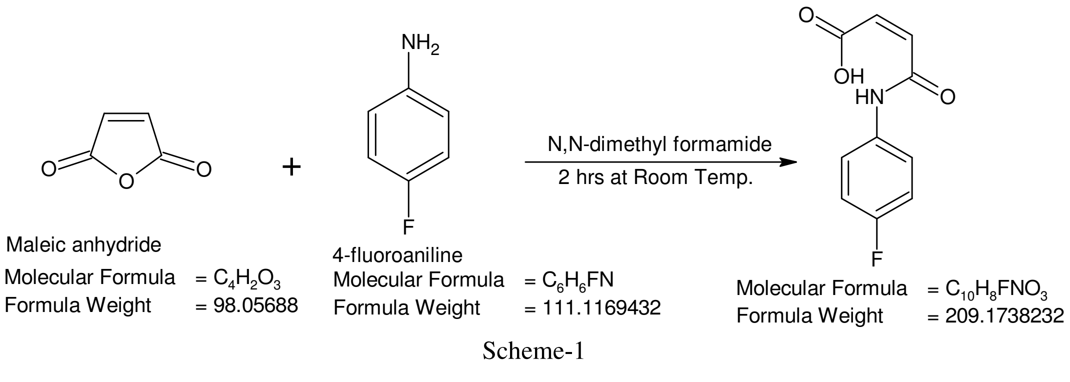
Copolymerization

Co-polymerization of N (4-fluoro phenyl maleimide) with MMA (preparation of CPFPM)

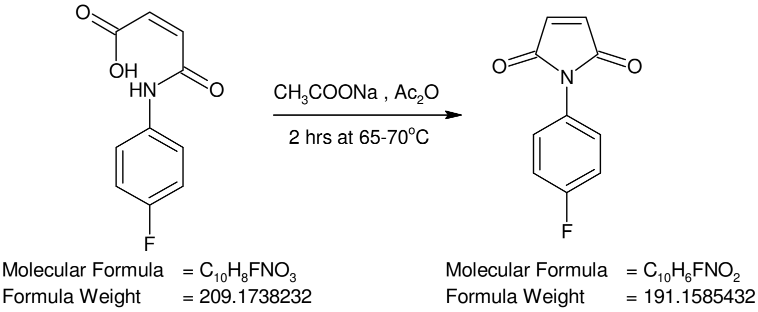
The equimolar amount of N(-4-fluoro phenyl maleimide) and MMA in THF solvent were taken in a round bottom flask. 20-30mg AIBN was added to the reaction mixture as a free radical initiator. This reaction mixture was heated at 60ºC for 24 hours. Equal amount methanol and water mixture was used to precipitate the copolymer. The crude product was dissolved in THF and reprecipitated in methanol this process was repeated twice to completely remove the unreacted monomer.

Measurements

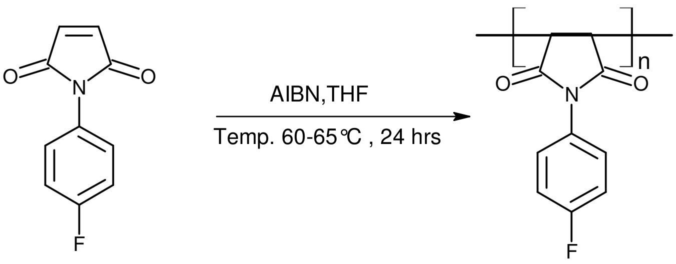
1H-NMR spectra of monomer and polymer were taken in DMSO-d6 on a Bruker DPX-200/DPX-300 spectrometer at 200/300 MHz. TMS was used as a internal reference. FT-IR spectra of the monomer and polymer were scanned in KBr pellets on Perkin Elmer IR spectrophotometer. The intrinsic viscosity measurements were carried out in DMF at 30±2°C by using Ubbelohde suspended level viscometer. Elemental analysis was carried out on Carlo-Erba elemental analyzer model 1106 series. The thermo gravimetric analysis was carried out in air at 10°C /min on a Mettler TA-3000 system, at a heating rate of 10°C/min from 0°C to 540°C.



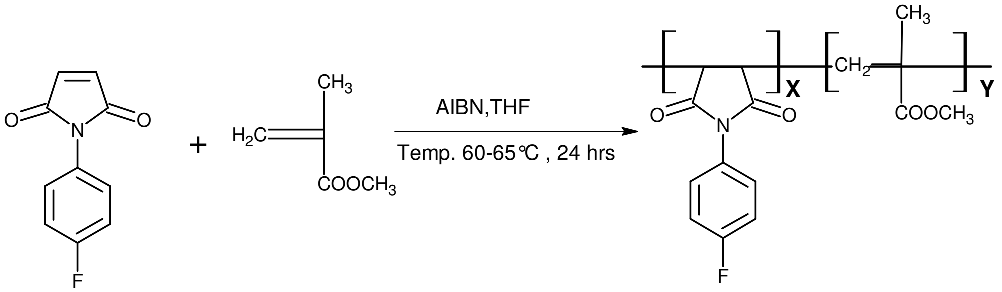
Scheme-1



Scheme-2



Scheme-3



Scheme-4

RESULTS AND DISCUSSION

Solubility

Table-1 summarizes the relative solubility of homopolymer (HPFPM) and copolymer (C- PFPM) in number of polar and non-polar solvents at 30°C. C- PFPM is soluble in THF, DMF, DMSO, dioxane, chloroform and ethyl acetate. Solubility behaviour in the later solvents depends on the composition of polymer.

Spectral characterization

The FT-IR spectra and 1H-NMR spectra of HPFPM shows following peaks and chemical shifts:

FT-IR spectra of copolymer shows absorption peak 1713 cm-1 and 1776 cm-1 is due to the symmetric and asymmetric stretching of the carbonyl group in imide ring and strong peak 1390 cm-1 is due to C-N-C stretch of imide ring. These characteristic bands confirmed that during the copolymerization imide ring is remained intact or the polymerization is not a ring opening polymerization. The sharp band at 1169 cm-1 is assigned to C-O stretching of ester. These characteristic bands confirmed that both the monomeric unit PFPM and MMA are present in copolymer and copolymerization is proceeding via vinyl group. In the spectra of CPFPM, characteristic signals due to both the monomer unit are present. The PFPM unit in copolymer was confirmed by signal 7.5 to 8.1 ppm due to aromatic phenyl ring and a signal at 4.0 ppm is attributed to the MMA unit. ^{1}H-NMR spectra also confirmed that the consumption of all vinyl groups of the comonomer due to signal of vinyl groups of both the monomer are absent in the spectrum and signals at 3.2 and 3.5 ppm appeared to $–[CH\text{-}CH]_n–$ protons and – OCH_3 protons.

Table-1: Solubility behavior of HPFPM and CPFPM in Polar and Non-polar solvents at 30°C.

Solvent	HPFPM	CPFPM
Dioxane	S	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	S	IS
Methanol	S	IS
Ethyl acetate	S	S

S=Soluble, IS=Insoluble

Physical Properties

The intrinsic viscosity [η] and molecular weight of the present polymer samples were determined. The value of η depends on molecular weight as well as on the size of polymer coil in given solution.

Table-2: Physical properties of HPFPM and CPFPM

Polymer Code	ρ(g/cm^3)	H(dl/g)	Mw(g/mol)
HPFPM	0.8780	0.189	5231
CPFPM	0.8390	0.168	22990

Thermal Properties

Polymaleimide is a potential heat and chemical resistant material, so Maleimide is widely used as a monomer to obtained modified polymeric system. The two step degradation was observed for polymaleimide in TGA at temperature of over 250ºC. The thermo grams were obtained by heating HPFPM and CPFPM in air 10°C/min. The results of percentage weight loss suffered from 100 ^{o}C to 540 ^{o}C at 100 intervals are shown in Table-4. 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-3

Table-3: Thermal behaviour of polymers

Polymer	T_i	T_{Max}	T_f	Residue at 500^o C
HPFPM	275	310	330	
	330	430	525	5%
CPFPM	230	285	355	
	355	435	510	12%

CONCLUSION

Synthesis, through free radical copolymerization of NPFPM with MMA has been investigated. The investigated copolymaleimide show excellent solubility in THF, DMF and DMSO. The characterization of copolymer was carried out through intrinsic viscosity, molecular weight distribution, FT-IR and ^{1}HNMR spectral analysis. Copolymer show good thermal stability and it degrade in two steps.

Table-4: Percentage weight loss of HPFPM and CPFPM at various temperatures from the TGA.

Polymer	200°C	300°C	400°C	500°C
	Weight loss (%)			
HPFPM	2	45	92	95
CPFPM	4	69	80	88

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