Synthesis, Characterization and Copolymerization of N-(phenylamino)maleimide with MMA

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Abstract: The free radical copolymerization of N-(phenylamino)maleimide (N-PAMI) was carried. The copolymerization with methyl methacrylate (MMA) was performed at 65°C with AIBN as the initiator in THF solvent. Resulting copolymer was characterized by density measurement, intrinsic viscosity, solubility, FT-IR & ¹H NMR spectroscopy. Effect of the solvent and time on copolymer yield was also investigated. The molecular weight of copolymer was determined by gel permeation chromatography (GPC). The thermal stability of copolymer was determined by Thermogravimetric analysis (TGA).

Keywords: N-(phenylamino)maleimide, free radical copolymerization, characterization

Introduction

Condensation type polyimides have certain disadvantages, like insolubility and infusibility^{1,2} and hence are difficult to process. To overcome these processing disadvantages polymaleimide have synthesized by employing the addition polymerization technique in solution. Most aromatic polyimides produced by the thermal solid-state phase imidization show insolubility and infusibility, which make processing difficult and limit applications. Addition type polyimides were developed mainly to overcome processing disadvantage³⁻⁷. Aromatic polyimides have been noted for excellent characteristics such as thermo oxidative stabilities and electrical properties as well as chemical resistance. The polymers have been

widely used for number of applications⁸⁻¹¹. N-substituted maleimides are known to copolymerized free radically¹²⁻¹⁸.

In order to investigate the possibility of obtaining better polymers from N-substituted maleimide. We have tried to prepare some new better polymer. In this paper we report the synthesis and characterization of copolymer of N-(phenylamino)maleimide with MMA (C-PAMI) using AIBN as a free radical initiator.

Experimental

Materials

Phenyl hydrazine was distilled and maleic anhydride was recrystallized from acetone. Methyl methacrylate (MMA) (CDH) were shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous CaCl_2 for 8 h and distilled. The head and tail fractions were discarded. AIBN (2,2'-azobis-isobutyronitrile (spectrochem.) was recrystallized twice from methanol prior to use. BPO (benzoyl peroxide) (CDH) were used as received. THF was purified by distillation after being refluxed for 2 h in the presence of sodium. DMF and methanol used in the present work were of analytical grade and were used as received.

Measurements

^1H -NMR spectra of monomer and polymer samples were taken in CDCl_3 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 samples were recorded on a shimadzu 8201 pc ($4000\text{--}400\text{ cm}^{-1}$) FT-IR spectrometer, using KBr pellet technique. The viscosities measurements were carried out in DMF at $30\pm 2^\circ\text{C}$, using on Ubbelohde suspended level viscometer. Elemental analysis was made on Carlo-Erba Model NA 500 series analyzer. The thermograms in air were obtained on a Mettler TA-3000 system, at a heating rate of $10^\circ\text{C}/\text{min}$.

Preparation of N-(phenylamino)maleimide (N-PAMI)

N-(phenylamino)maleimide was synthesized in two steps from maleic anhydride and phenyl hydrazine. (described below and shown in scheme-1)

N-(phenylamino)maleamic acid (N-PAMA)

Phenyl hydrazine (10.8 gm, 0.1mole) in 30 mL DMF was gradually added to well stirred DMF/maleic anhydride (9.8gm, 0.1 mole) in flat bottom flask and then stirred for 3 h at room temperature. This solution is poured in crushed ice water. The yellow colored solid (N-PAMA) is precipitated. This precipitate was filtered and dried at 70°C . It was recrystallized from methanol solvent to obtain pure N-PAMA in 75% yield, m.p. 220°C . The IR spectrum showed absorptions at 3527 (carboxylic acid O-H), 1560 (amide N-H), 3410, 3069 (aromatic and alkene C-H), 1708 (carboxylic acid and amide), 1278 (carboxylic acid C-O), 1618 ($\text{C}=\text{C}$ aromatic, $911\text{ (CH=CH)}\text{ cm}^{-1}$. ^1H -NMR (300MHz, TMS, CDCl_3 , δ ppm): 7.5-6.8(2d, $j=7.5$ Hz in phenyl), 6.16 (s, 2H, CO-CH=CH-CO), 3.27(s, 1H in N-H), 3.74(N-H singlet), 11.40(s, 1H, COOH).

N-(Phenylamino)maleimide (N-PAMI)

Cyclodehydration was carried by treating N-PAMA with conc. H_2SO_4 and P_2O_5 carried out to maleimide. In flat bottom flask containing DMF solution of N-PAMA (20.6 gm, 0.1 mole) in 30 mL DMF, to this DMF (30mL) solution of P_2O_5 (7.4 gm) & conc. H_2SO_4 (1 mL) was added gradually with stirring. This solution was stirred for 2 h at 70°C . The reaction

mixture was cooled and poured into crushed ice water to obtain the yellow color precipitate of N-PAMI. The precipitate was filtered and washed several times with water and finally dried. N-PAMI was recrystallized from methanol solvent. The yield was 72% and melting point 215°C. The IR spectrum showed absorption frequencies 3062.2 (aromatic and alkene C-H stretch), 3433 (-NH stretch), 1778.4 and 1716.7 (symmetric and asymmetric stretch of C=O in a five member imide ring), 1596.8, 1517.0 and 1495.8 (C=C aromatic), 1416.2 (C-N stretch) cm^{-1} . ^1H NMR (300M Hz, TMS, CDCl_3 , δ ppm): 7.5-6.8 (2d, 4H phenyl) 3.74 (s, 1H, N-H), 6.3 and 7.1 (s, 2H, $\text{O}=\text{C}-\text{CH}=\text{CH}-\text{C}=\text{O}$).

Polymerization Procedures

Calculated amount of monomer N-PAMI with MMA in 70mL THF solvent were taken in a round bottom flask. Then 20mg AIBN was added to the reaction mixture as a free radical initiator. The copolymerization reaction was carried out at 65°C for 24 h. Polymer samples were isolated in water containing 20% methanol. The copolymer were purified by first dissolving in THF and then, reprecipitating in excess quantity of methanol–water mixture. The precipitated copolymer were washed several times and dried at 60°C under vacuum.

Table 1. Radical copolymerization of N-PAMI and MMA in THF at 65°C

Polymer code	Feedmole fraction of N-PAMI	Polymerization time (h)	Yield (%)	N (%)	Appearance
C-PAMI	0.5	24	37.07	4.57	Light yellow

Results and Discussion

1. Solvent - Initiator System

Free radical copolymerization of maleimides is known to be useful on the synthesis of polymaleimides. This method was applied to their preparation from N-PAMI and vinyl monomers to find suitable condition in which to prepare copolymaleimide with relatively high yield. The effect of initiator & solvent were investigated in details. The effect of reaction solvents and initiator on yield of C-PAMI was formed in different pairs of solvent initiator is summarized in Table 2.

Table 2. Radical copolymerization of N-PAMI and MMA in various solvent-initiators system

Solvent	AIBN	BPO
	Yield of C-PAMI(%)	Yield of C-PAMI (%)
THF	37.07	36.01
DMF	22.34	21.30
Ethylacetate	26.94	28.20
<i>p</i> -Dioxane	29.43	30.40
Acetone	31.20	30.10

The percentage yield of the C-PAMI in the AIBN –DMF system was poor compared to AIBN- dioxane and BPO- dioxane. AIBN-Acetone system gave better yield of C-PAMI over the AIBN-EA & BPO-EA system. AIBN –THF system of copolymerization gave better yield then other solvent–initiator system including BPO-THF system. Examination of all the aspect AIBN-THF system was most suitable for the present copolymerization process.

2. Effect of Time on polymer yield

The effect of reaction solvents and time of stirring on yield of C-PAMI is summarized in Table 3. Table 3 reveal that N-PAMI gave better yield of copolymerization in 24 h in THF solvent.

Table 3. Radical copolymerization of N-PAMI and MMA in different time.

Solvent	C-PAMI		Yield (%)	
	12 h	24 h	36 h	48 h
THF	12.01	37.90	39.07	40.01

3. Solubility

Table 4 summarizes the relative solubilities of copolymer samples in number of polar and non-polar solvents at 30°C. The investigated copolymer samples are soluble in Acetone, Cyclohexanone, THF, DMF, Dichloromethane, DMSO, and solvent and insoluble in CCl₄, Xylene, Hexane Ethanol, Methanol and Water. Solubility behaviour in the later solvents depends in the solvent taken.

Table 4. Solubility behaviour of monomer, homopolymer and copolymer in polar and non-polar solvents at 30°C.

Solvent	N-PAMI	C-PAMI
Acetone	S	S
Cyclohexanone	S	S
<i>p</i> -Dioxane	IS	S
THF	S	S
DMF	S	S
Dichloromethane	S	S
DMSO	S	S
Chloroform	S	S
CCl ₄	IS	S
Xylene	IS	IS
Toluene	IS	PS
Hexane	PS	IS
Methanol	IS	IS
Water	IS	IS

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

4. Intrinsic Viscosity [η]

Intrinsic viscosity [η] is a measure of hydrodynamic volume and depends on molecular weight as well as on the size of the polymer coil in a given solution. The value of average η in DMF solution at 30°C is listed in Table 5. The value of η is 0.240 dL/gm for C-PAMI. The value of η depends on the composition of N-PAMI.

Table 5. The Intrinsic viscosity, density and molecular weight of C-PAMI.

Polymer	Density ρ (g/cm ³)	η (dL/g)	M_w
C-PAMI	0.8491	0.240	25581.4

5. Molecular weight

Molecular weight of C-PAMI is determined by GPC method using THF solvent. The number average molecular weight of C-PAMI is 900.1. The weight average molecular weight of C-PAMI is 1730.1. The average molecular weight of C-PAMI is 25581.4.

6. Density

The densities of solid copolymer samples were determined at 30°C by displacement method with single stem pycnometer¹⁹ using water as a non-solvent. The density of C-PAMI is given in Table 4. The density of C-PAMI is 0.8491 g/cm³. The result indicates that density of C-PAMI is less than water.

7. Spectral characterization

In this study ¹H-NMR and FT-IR spectroscopy were used to characterize the copolymer. In the FT-IR spectrum, the major characteristic absorption bands are observed at 3319 cm⁻¹ (-NH stretch), 1780.3, and 1724.2 cm⁻¹ (C=O symmetric and asymmetric stretch in a five member imide ring and C=O stretch of ester), 1602.7, and 1496.9 cm⁻¹ (aromatic, C=C and amide group). The imide group is also confirmed from the bands observed at 1495.8 (Ar-N stretch), 1416.2 (C-N stretch), 1164 (C-N-C), 1170 and 760 cm⁻¹. The broad medium intense

band at 1596.8cm^{-1} , strong intense band at 1571.0cm^{-1} and a medium band at 1495.8cm^{-1} correspond to the aromatic ($\text{C}=\text{C}$) band. The broad stretching bands at 3433.6cm^{-1} represent secondary amine ($-\text{NH}$). These characteristic bands confirm that units of both the monomers N-PAMI and MMA are present in the copolymer samples. Compared with the IR spectra of monomers, it was found that the characteristic peaks of the double bond disappeared in the spectrum of the copolymer, for example, 911cm^{-1} for N-PAMI.

The $^1\text{H-NMR}$ spectra of the copolymer showed the following chemical shifts. The δ at 7.27-6.91 ppm is 5 H of aromatic phenyl ring. A δ at 4-5-5.0 ppm appeared for 2H of $-(\text{CH}-\text{CH})-$ in the polymer main chain and δ observed at 3.4-4.6 ppm corresponds to overlapping of 1H in $-\text{N-H}$ group of amino phenyl maleimide segment and 3H ($-\text{OCH}_3$) of MMA segment. The δ in the range 0.8-1.4 ppm is of 2H of methyl group while at 1.43–2.20 ppm for 2H of methylene group. $^1\text{H-NMR}$ spectrum also confirmed the consumption of all the vinyl groups of the comonomers because absorptions of vinyl groups of both monomers are absent in the spectrum, for example, 6.8 ppm for vinyl protons of N-PAMI and 5.0-6.0 pm for MMA. This indicated that the polymerization happened via the opening of the double bond.

8. Thermal Properties

It is well known that polymaleimide is potential heat and chemical resistant material so maleimide is widely used as a monomer for modified polymeric systems. Only single step degradation at temperature of over 300°C was observed for polymaleimide in TGA. The thermograms were obtained by heating copolymer sample in air at $10^\circ\text{C}/\text{min}$. The typical TGA curve was obtained of C-PAMI. The results of percentage weight loss suffered from 100°C to 600°C at 100 Intervals are furnished in Table 7.

The initial decomposition temperature T_i , temperature for maximum weight loss T_{max} , and final decomposition temperature T_f of first degradation step of are given in Table 6. The copolymer C-PAMI is decomposing through a one step procedure. As the copolymer sample content of N-PAMI is 50% the initial decomposition temperature (T_i) is 220°C and weight loss for the first step became larger. The first step weight loss was range to 60 to 75%. The weight loss of C-PAMI upto 600°C is 89-90%. Table 7 reveals that weight loss was below 0.8 to 8 % up to 300°C in copolymer sample

Table 6. Thermal Behaviour of copolymer

Polymer	T_i ($^\circ\text{C}$)	T_{max} ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	Residue at 500°C
C-PAMI	220	300	330	11%
	330	400	550	

Table 7. Percentage weight loss of copolymer at various temperatures from the TGA.

Polymer	200°C	300°C	400°C	500°C	600°C
	Weight loss, %				
C-PAMI	2	49	84	89	90

Conclusions

Synthesis, through free radical copolymerization of N-PAMI with MMA has been investigated. The most suitable initiator-solvent pair for the copolymerization was found to

be AIBN-THF. The investigated copolymaleimide show excellent solubility in THF, DMF, DMSO, chloroform, dichloromethane, Acetone and Cyclohexanone. The characterization of copolymer was carried out through intrinsic viscosity, molecular weight distribution, elemental analysis, FT-IR and ^1H -NMR spectral analysis. Copolymer show good thermal stability and it degrade in two-steps.

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