Synthesis and Characterization of Some New Thermal Stable Polymers - Polymerization of N-[4-N'-(Benzylamino-carbonyl)phenyl]maleimide

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Abstract: This article describes the synthesis and characterization of homopolymer (H-BCPM) of N-[4-N'-(benzylamino-carbonyl) phenyl] maleimide (N-BACPMI) and copolymer (C-BCPM) of N-BACPMI with *n*-butyl acrylate (BA). The new monomer was synthesized from *p*-aminobenzoic acid, maleic anhydride and benzylamine. The homopolymerization of N-BACPMI is initiated by free radical using AIBN in THF solvent at 65 °C. Radical copolymerization of N-BACPMI with BA, initiated by AIBN, was performed in THF solvent using equimolar amount. Effect of the different free radical initiator AIBN, BPO and solvents *p*-Dioxane, THF, DMF and DMSO was studied. Homopolymer and Copolymer were characterized by intrinsic viscosity, solubility test, FT-IR, ¹H-NMR spectral analysis and elemental analysis. Thermal behaviour was studied by Thermo gravimetric analysis.

Keywords: Radical polymerization, N-[4-N'-(benzylamino-carbonyl) phenyl] maleimide, *n*-butyl acrylate, Characterization.

Introduction

Currently, polymers with defined architecte and controlled composition are of considerable interest for their academic and industrial uses¹⁻³. There is a considerable interest not only in the synthesis of new type of the plastic materials but also in the modification of exiting polymers in order to vary its properties to meet requirements for new

applications under unusual working conditions⁴⁻⁶. Most aromatic polyimides produced by the thermal solid-state phase imidization show insolubility and infusibility, which make processing difficult. These undesirable properties, which limit wider application of the polyimides, are due to their chain rigidity as well as to poor defined molecular architectures. Addition type polyimides were developed mainly to overcome processing disadvantages⁷⁻⁹. During the past several years many publications appeared describing the chemical modification of various vinyl polymers such as styrene or methyl methacrylate by an addition N-substituted maleimide¹⁰⁻²². In order to investigate the possibility of obtaining better polymers from N-substituted maleimide, we report here the synthesis of N-[4-N'-(benzylamino-carbonyl) phenyl] maleimide monomer and its polymerization and copolymerization with n-butylacrylate. It was observed that such copolymers have better thermal stability than the polymers of vinyl monomers. However, polymerization of N-BACPMI has not been investigated. The goal of this study was assessment of polymerization of N-BACPMI, whose incorporation into the backbone chain could present a considerable and promising interest. The N-BACPMI monomer is a five member planer ring which completely hinder the rotation of the imide residue around the back bone chain of the macromolecules and expected to produce copolymers with a great structures stiffness as well as higher thermal stabilities. The physical, spectral and thermal properties have been studied in order to characterize the homo and copolymer.

Experimental

Materials

p-Aminobenzoic acid and maleic anhydride were recrystallized from acetone. n-Butylacrylate (CDH) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous CaCl₂ for 6 h and distilled²³. 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) was used as received. THF was purified by distillation after being refluxed for 2 h in the presence of sodium²³. Dioxane and DMSO were used after distillation. 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 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 (4000-400 cm⁻¹) FT-IR spectrometer, using KBr pellet technique. The viscosity measurements were carried out in DMF at 30±0.2 °C, using an 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 °C/min

Preparation of N-[4-N'-(benzyl amino-carbonyl)phenyl]maleimide (N-BACPMI)

N-BACPMI monomer was synthesized in four steps²⁴⁻²⁶ from maleic anhydride, *p*-aminobenzoic acid and benzylamine (described below and shown in Scheme 1).

N- (4-Carboxyphenyl) maleamic Acid (*p*-CPMA)

A solution of maleic anhydride (19.62g, 0.2 mol) in DMF was gradually added over a period of 10 minute to a well-stirred solution of *p*-aminobenzoic acid (27.42 g, 0.2 mol) in DMF.

Then the mixture was stirred for 5 h at room temperature. The resulting solution was poured into a large amount of crushed ice to precipitate crude *p*-CPMA. The crude *p*-CPMA was filtered, dried and then recrystallized from ethanol to obtain pure *p*-CPMA in 85% yield, mp 222 °C (lit. mp..225-226 °C)²⁰. The IR spectrum showed absorptions at 3500-2500 (carboxylic acid O-H), 3317, 1544 (amide N-H), 1697 (carboxylic acid and amide), 1288 (carboxylic acid C-O), 848 (CH=CH), 675 (C-H bending) in cm⁻¹. ¹H-NMR (300MHz, TMS, DMSO-*d*₆ δ ppm): 10.45 (s, 1H, COOH); 7.4 & 7.8 (2d, *j*=8.58 Hz in phenyl); 6.16 (s, 2H, CO-CH=CH-CO); 3.27 (s, 1H in -NH); 11.45 (s, 1H, COOH).

Scheme 1.

N-(4-Carboxyphenyl) maleimide (*p*-CPMI)

A mixture of 23.5 g (0.1mol) *p*-CPMA, 16.4g (0.2mol) sodium acetate and 120mL acetic anhydride were stirred for 2 h at 55-60 °C. Cooled reaction mixture was poured into large amount of crushed ice, light yellow mass obtained of *p*-CPMI was filtered and dried at 60-70°C and the recrystallized from methanol obtaining the product in a 75% yield with mp 231°C (lit. mp. 225-228°C²⁷ and 231°C²⁸). The IR spectrum showed absorption 3500-2500 (Carboxylic acid O-H), 1774, 1714 (C=O stretch, 5-membered imide ring), 1215 (Carboxylic acid C-O), 1598, 1514(Aromatic C=C), and 952, 698 (CH=CH) cm⁻¹. ¹H-NMR (300MHz, TMS, DMSO-*d*₆ δ ppm): 12.45 (s, 1H, COOH); 8.07 and 8.03 (2d, 4H, Phenyl); 7.5 and 7.9 (s, 2H, OC-CH=CH-CO).

N-[4-(Chlorocarbonyl) phenyl] maleimide (*p*-CPMIC)

A mixture of *p*-CPMI (17.1430gm, 0.079mol) and thionyl chloride (150 mL, 2.07 mol) was refluxed at 80°C for 2 h. The unreacted thionyl chloride was evaporated off and residual product was recrystallized from benzene to obtained pure light yellow crystals of acid chloride. It was obtained in 80% yield, mp 157°C (lit. mp 153-157°C²⁷ and 153°C³⁰). The IR spectrum showed absorption at 1747 (COCl), 1747, 1716 (CONCO), 1610 (C=C), 883, 840 (CH=CH) cm⁻¹. ¹H-NMR (300MHz, TMS, DMSO-*d*₆ δ ppm): 8.07 and 8.03 (2d, 4H in phenyl); 7.5 and 7.9 (s, 2H, OC-CH=CH-CO).

N-BACPMI

A benzene solution of benzylamine (0.5mol in 100ml benzene) was added drop wise to a CPMIC (11.75gm 0.5mol) solution in benzene (100mL) at 0-5°C and the mixture was stirred at room temperature for 2 h. The precipitated product was filtered, washed with water, dried and then recrystallized twice from ethanol to obtain pure N-BACPMI in a 62% yield, mp 165°C. The purity and structure of the monomer was ascertained by elemental (C, H, N) analysis, IR and ¹H NMR study. Anal.calcd.for C₁₈H₁₄O₃N₂, C, 70.59; H, 4.57; N, 9.15; Found C, 69.98; H, 4.01; N, 8.68. FT-IR: 3400-3300 (-NH), 1633, 1508, (CONH), 1770, 1709 (CONCO) 1399(C-N), 950, 694 (CH=CH) cm⁻¹. ¹H NMR (300 MHz, TMS, DMSO-*d*₆, δ ppm) 7.20 (s, 2H, CH=CH); 8.01-7.98 (d, 2H in phenyl ring meta- to maleimido); 7.80-7.77 (d, 2H in phenyl ring ortho- to maleimido); 9.48 (s, 1H, CONH); 7.52-7.47 (d, 2H in phenyl ring ortho- to amide); 7.38-7.29 (t, 2H in phenyl ring meta- to amide); 4.51 (s, 2H in methylene group) and 7.28-7.25 (t, 1H in phenyl ring para- to amide).

Polymerization*Homopolymerization*

Radical homopolymerization of N-BACPMI (0.03 mol, 9.18gm), were carried out with AIBN as a free radical initiator in THF (120mL), in a round bottom flask. Reaction mixture was refluxed at 65°C for 24 h. The homopolymer (H-BCPM) was isolated by precipitation in methanol containing water. The precipitated homopolymer was washed with methanol several times and dried in a vacuum oven. A summary of polymerization conditions and physical characteristics of H-BCPM are presented in Table 1. Various homopolymer samples were obtained using different solvent-initiator combination. The percentage yields of homopolymer samples, using different solvent/initiator systems, are presented in Table 2.

Copolymerization

The reaction mixture was carried out in the round bottom flask in equimolar amount of N-BACPMI and n-butylacrylate in 110mL THF were refluxed after adding 25 mg AIBN at 65°C for 12 h. The copolymer (C-BCPM) was precipitated in methanol and water mixture. The precipitated copolymer was filter and washed with methanol several times and dried. A summary of polymerization conditions and physical characteristics of C-BCPM are presented in Table 1.

Various copolymer samples were obtained using different solvent-initiator combination. The percentage yield of copolymer samples, using different solvent/initiator systems are presented in Table 2.

Table 1. Radical polymerization and copolymerization of N-BACPMI and *n*-butyl acrylate in THF at 65°C.

Polymer Code	Feed mol fraction of N-BACPMI	polymerization Time (h)	Yield (%)	%N	[η] (dL/g)	Appearance
H-BCPM	1.0	24	46.58	8.68	0.157	Cream
C-BCPM	0.5	12	51.65	6.35	0.200	white

Results and Discussion

Solvent-Initiator System

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

Table 2. Percentage yield of homo and copolymaleimide in various solvent-initiator systems.

Solvent	AIBN		BPO	
	H-BCPM Yield (%)	C-BCPM Yield (%)	H-BCPM Yield (%)	C-BCPM Yield (%)
THF	46.58	51.65	45.98	49.05
<i>p</i> -Dioxane	45.26	44.26	45.69	47.04
DMF	28.45	35.25	27.58	39.26
DMSO	43.25	48.02	38.14	49.28

The percentage yield of the H-BCPM in the AIBN-DMF system was poor compared to AIBN-dioxane and BPO-dioxane. AIBN-DMSO system gave better yield of C-BCPM over the AIBN-dioxane & BPO-dioxane system. AIBN-THF system of both polymerizations 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 homo & copolymerization process.

Effect of Time on polymer yield

The effect of reaction solvents and time on yield of H-BCPM and C-BCPM was formed in different time is summarized in Table 3.

Table 3. Percentage yield of homo and copolymaleimide in different time.

Solvent	H-BCPM Yield (%)				C-BCPM Yield (%)			
	12 h	18 h	24 h	30 h	12 h	18 h	24 h	30 h
THF	35.65	40.56	46.58	47.56	51.65	52.52	53.25	53.69

Table 3 reveal that N-BCPMI gave better yield of homopolymerization in 24 h in THF solvent and copolymerization in 12 h.

Solubility

Table 4 summarizes the relative solubilities of homo and copolymer samples in number of polar and non-polar solvents at 30 °C. The investigated homo and copolymer both samples are soluble in THF, DMF, DMSO, ethyl acetate, acetone, chloroform, dichloromethane and Cyclohexanone. Individual homopolymer is soluble in *p*-dioxane and partially soluble in carbon tetrachloride. Solubility behaviour in the later solvents depends on the composition of polymer. The solubility of homopolymer is more than copolymer in the solvent taken.

Table 4. Solubility Behaviour of monomer, homopolymer and copolymer in Polar and Non-polar Solvents at 30°C.

Solvent	N-BACPMI	H-BCPM	C-BCPM
Acetone	IS	S	S
Cyclohexanone	IS	S	S
Dioxane	S	S	IS
THF	S	S	S
DMF	S	S	S
Dichloromethane	IS	S	S
DMSO	S	S	S
Chloroform	IS	S	S
CCl ₄	IS	PS	IS
Xylene	IS	IS	IS
Toluene	IS	IS	IS
Methanol	IS	IS	IS

S=Soluble, IS= Insoluble, PS=Partially Soluble

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 values of average [η] in DMF solution at 30 °C are listed in Table 1. The value of [η] decreases from 0.200 to 0.157 dL/gm for copolymer to homopolymer. The value of [η] depends on the composition of N-BACPMI. Intrinsic viscosity of homopolymer is less than copolymer. It's indicating the content of N-BACPMI is increased then value of η is decreased.

Spectral characterization

The FT-IR spectrum and ¹H-NMR spectrum (300MHz in DMSO- *d*₆) of H-BCPM are shown following peak and chemical shift. The absence of a sharp band at 950cm⁻¹ and chemical shift δ at 7.32 ppm due to CH=CH in a monomer having a vinyl group, such as monomer N-BACPMI, indicates the formation of polymer via vinyl group polymerization^{29, 30}.

The presence of absorption bands at 1770 and 1715 cm⁻¹ due to symmetric and asymmetric stretching of C=O in the five member imide ring indicates that the imide ring remained intact in the polymerization. The imide group is also confirmed from the bands observed at 1452(Ar- N stretch), 1368 (C-N stretch), 1164 (C-N-C), 1115 cm⁻¹ and 750 cm⁻¹. The broad medium intense band at 1668cm⁻¹, strong intense band at 1508cm⁻¹ and a medium band at 1539 cm⁻¹ correspond to the amide group. The broad stretching band at 3309 cm⁻¹ represent secondary amine (-NH).

The δ observed at 7.23 ppm due to CH=CH in the monomer has shifted to 3.4-4.1 ppm in the polymer, as a result of the formation of a semi flexible poly (substituted methine) - [CH-CH]_n- group³¹. The δ for methine -(CH-CH)- protons has been reported in the range from 3.0-5.0 ppm depending upon the substitution in maleimide. The value of δ in the range 3.0-4.0 for poly [N- [4-N'- (α -methylbenzyl) aminocarbonyl phenyl] maleimide²⁶, 3.5-4.5 for poly (N- alkyl substituted phenyl) maleimide³¹ and poly [N-[4-(cholesteroxy carbonyl phenyl) maleimide]³² have been reported . The broad peak at 7.0 –8.1 ppm corresponds to 9 Ar-H.

The major characteristic absorption bands are observed at 3400- 3300 (broad, -NH stretch), 1774, 1716 (C=O symmetric and asymmetric stretch in a five member imide ring and C=O stretch of ester), 1603, 1528 (aromatic, C=C and amide group). These characteristic bands confirm that units of both the monomers N-BACPMI and *n*-butyl acrylate are present in the copolymer samples.

The ¹H NMR spectra of the copolymer showed the following chemical shifts. The δ at 7.86-7.84 ppm is of 2 Ar-H, ortho- to N of imide group while at 7.65-7.62 ppm for 2 Ar-H, meta- to N-of imide group. The δ at 7.37-7.36 ppm is for 2 Ar-H, ortho- to N of the amide group; at δ 7.3-7.5 ppm is for 2Ar-H , *para*- to N of the amide group and 7.26-7.23ppm is for 2 Ar-H, *meta*-to N of amide group . A δ at 9.55 (broad) ppm appeared for 1H in -CONH- group of N-BACPMI segment and δ observed at 4.47 ppm is 2H in -CH₂ of benzyl segment. The δ observed at 3.4-3.7 ppm corresponds to overlapping of 2H -(CH-CH)- in the polymer main chain and 2H (-OCH₂) of BA segment. The δ in the range 1.0-2.4 ppm is of 2H of methylene group and 1H of -CH- group while at 0.96 –1.57 ppm for 7H of butyl group except -OCH₂.

Thermal Properties

It is well known that polymaleimide is potential heat- and chemical-resistant material, so maleimide is widely used as a comonomer 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 homopolymer and copolymer sample in air 10°C/min. the typical TGA curve. The results of percentage weight loss suffered from 100°C to 600°C at 100 intervals are furnished in Table 6.

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 5. The results in Table 5 indicate that the relative thermal stability on the basis of *T_i* follows on the order H-BCPM>C-BCPM.

As the content of N-BACPMI in the feed is 100% in the homopolymer began to decompose at higher *T_i* and weight loss for the first step became smaller. The first step weight loss ranged from 40-42 %. The weight loss for the second step became larger increasing from 55-60%. The total weight loss of H-BCPM upto 600°C is 70%.

The copolymer C-BCPM decomposes through a two-step procedure. As the copolymer sample content of N-BACPMI is 50%, the copolymer began to decomposition at lower *T_i* and weight loss for the first step became larger as compared to homopolymer. The first step weight loss was range to 60 to 65%. The weight loss for second step is 23 to 30%. The total weight loss of C-BCPM upto 600°C is 90-95%.

Table 6 reveals that weight loss was below 0.8 to 8% up to 300°C in copolymer sample & 100% content of N-BACPMI feed in homopolymer weight loss was below 0.1 to 2 % up to 300°C. The results in Table 5 indicate that the thermal stability tends to increases from the copolymer to homopolymer.

Table 5. Thermal behaviour of homopolymer and copolymer.

Polymer		T _i (°C)	T _{max} (°C)	T _f (°C)	Residue at 500(°C)
H-BCPM	I	288	360	415	45
	II	415	575	690	
C-BCPM	I	442	367	526	25
	II	526	593	660	

Table 6. Percentage weight loss of homo and copolymer at various temperatures from the TGA.

Polymer	200 °C	300 °C	400 °C	500 °C	600 °C
	Weight loss, (%)				
H-BCPM	0.7	25	45	55	70
C-BCPM	0.6	35	73	75	95

Conclusions

Synthesis, through free radical polymerization, homopolymerization of N-BACPMI and copolymerization of N-BACPMI with n-butylacrylate has been investigated. The most suitable initiator-solvent pair for the homo and copolymerization was found to be AIBN-THF. The investigated homo and copolymaleimide show excellent solubility in THF, DMF, DMSO, ethyl acetate, chloroform, dichloromethane and cyclohexanone. The characterization of homo and copolymer was carried out through elemental analysis, IR and ¹H-NMR spectral analysis. Homopolymer show good thermal stability then copolymer and it degrade is two-step.

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