Synthesis and Characterization of Poly (*p*-Phenylene Methylene) Using Sulphated Multiwalled Carbon Nanotubes

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Abstract: **Multiwalled carbon nanotubes (MWCNTs) were activated using concentrated sulphuric acid, to generate acid functionalities. These materials were evaluated for their catalytic activity in the synthesis of poly (p-phenylene methylene) (PPM) via polymerization of benzyl alcohol under different experimental conditions. The polymeric product was isolated and analyzed by GPC, PXRD, FT-IR, ^{1}H NMR, ^{13}C NMR, and SEM techniques. The isolated yield of PPM was 93.1%. The molecular weight and polydispersity index of isolated PPM were respectively 1711 g/mol and 6.56. Further the catalyst was recycled upto 5 times without any loss in its activity. In order evaluate the relationship between the catalytic activity and physicochemical properties, the catalysts were characterized by PXRD, FT-IR, BET surface area, SEM-EDS techniques.**

Keywords: **Multiwalled carbon nanotubes, catalytic activity, benzyl alcohol, Poly (p-phenylene methylene).**

I. INTRODUCTION

Polymer plays a crucial role in the emergence of the modern world. They find a numerous applications in various industries such as pharmaceutical, automobile, textile, bioregulation and biosensors testing devices [1]-[3]. Polyphenylene methylene (PPM) or Polybenzyl is an excellent polymeric material which is made up of alternating sequence of phenylene and methylene units. This polymer has special properties like low dielectric constant, high thermal stability and solvent resistance. Due to these special properties of PPM, it is widely used as adhesives, photoresists and polymeric blend materials in polymer industries [4].

In 1854 Cannizzaro,[5] reported that a polymeric material was obtained when benzyl alcohol was reacted upon acidic compounds such as BF_3, H_2SO_4 or P_2O_5 and later this polymeric material was recognized as low molecular weight poly (p-phenylene methylene), PPM. Subsequently, keeping in view of the industrial importance of PPM, many have reported diverse approaches for the synthesis of PPM and its derivatives via different acid catalysed reactions. For instant the following are a few representative reports on this subject,

which highlight the importance of acid catalysts. In 1970, G Montaudo et.al.[6] has studied kinetics of polycondensation of benzyl chloride and its derivatives at different temperatures in the presence of Lewis acids such as $SnCl_4$ and $AlCl_3$ as catalysts. Detail structures and thermal degradation of polybenzyls synthesized from the benzyl compounds using Friedel-crafts Lewis acid catalysts was reported by Bryan Ellis and P.G.White [7]. Linear soluble polybenzyls were synthesized by the polycondensation of 1,2,4,5-tetra substituted benzenes with formaldehyde using $CHCl_3$/trifluroacetic acid as the medium[8]. An attempt was made by R Eric Banks and co-workers to study the polymerization of benzyl alcohol using anhydrous HF as a catalyst at low temperatures [5]. H_2SO_4/P_2O_5 catalysed synthesis of soluble Poly (*p*-phenylene methylene) from Tribenzyl borate was reported by Niyazi Bicak et.al [9]. A few other attempts were made to prepare PPMs via. Reductive coupling [10] and ring opening reactions [8]. A systematic study of the literature on PPM clearly indicates

- The advantages and disadvantages of the reported methods.
- Dependence of the chemical, physical and mechanical properties of the polymeric material on its formulation,
- Generation of new functions and hence the applications of polymers due to little changes in structure of formulation of the polymer and [11].
- Apparent scope for further studies to develop catalysts which are economical, more efficient and ecofriendly for the synthesis of PPMs.

Our research interests are in the area of development of new catalytic materials for the synthesis of industrially important organic chemicals. Herein, we wish to report for the first time the catalytic activity of acid activated MWCNTs in the synthesis of PPM under mild and environmentally benign experimental conditions via polymerization of benzyl alcohol and report a plausible structure –activity relationship of the catalyst in the polymerization reaction.

II. EXPERIMENTAL

A. Materials

MWCNTs used in this work were obtained from Nanocyl, Belgium. Benzyl alcohol, Sulphuric acid and Dichloromethane of A.R grade were purchased from E-Merck.

B. Preparation of S-MWCNTs and characterization

0.1g commercial MWCNTs was sonicated with 10ml of concentrated H_2SO_4 for 3h and then mixed well in 1L of deionized water. The solid was separated by filtration, washed with DI water until the p^H of the filtrate was neutral to litmus test and dried at 110^oC for 24 h in an air oven. The material thus prepared is henceforth represented as catalyst and abbreviated as S-MWCNTs.

C. Synthesis and characterization of Poly (p-phenylene methylene) PPM polymer

The catalytic activity of the S-MWCNTs was investigated in the polymerization of benzyl alcohol into poly (p- phenylene methylene) (Scheme 1).
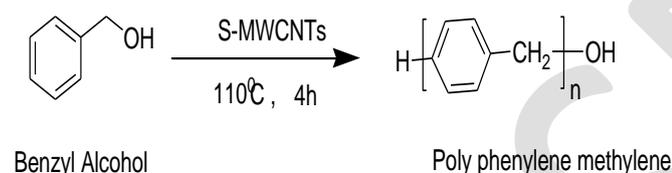
Scheme 1: Polymerization of benzyl alcohol to PPM in the presence of S-MWCNTs catalysts.

In a typical procedure 4 ml of benzyl alcohol was mixed with 100 mg of S-MWCNTs in a 100 ml R.B. flask and refluxed over a heating mantle at 110 ^{o}C for 4 h. The reaction mixture was cooled to room temperature; a thick brownish pasty mass was obtained. This was extracted along with the catalyst using CH_2Cl_2. The catalyst was separated by centrifugation. Further the effect reaction conditions such as the amount of the catalysts, temperature and duration of the reaction was investigated. The product was recrystallized and analyzed by GPC, PXRD, FT-IR, ^{1}HNMR, ^{13}CNMR and SEM techniques. GPC result was obtained by using Turbo matrix-40, Perkin Elmer model. ^{1}HNMR and ^{13}CNMR spectra of the polymeric product were recorded from Bruker instrument. SEM image was obtained using Philips Instrument.

D. Characterization of S-MWCNTs for its physicochemical properties.

In order to evaluate the relationship between the textural properties of the catalyst and its catalytic activity, the catalytic materials were characterized by appropriate analytical techniques such as PXRD, FT-IR, BET surface area, SEM-EDS. Surface acidity was determined by n-butylamine titration [12] (The detail of the method is given as a supplementary data). Powder X-ray diffraction (PXRD) patterns were recorded on a Panalytical Xpert pro X-ray diffractometer using Cu Kα radiation (λ = 0.154 nm) in the 2θ range of 5° to 70° at 40 kV and a scanning rate of 2°/min. Infrared spectra (FT-IR) were recorded from a Nicolet Model Impact 400D FT-IR spectrometer with 4 cm^{-1} resolution by KBr pellet technique. BET surface area was determined from N_2 adsorption data acquired on a Micromeritics TriStar 3000 instrument. Elemental composition and morphology of the materials were determined by EDS - SEM techniques using Quanta 200 FEI instrument.

III. RESULTS AND DISCUSION

1) Catalytic activity studies:

When benzyl alcohol was refluxed for 1 - 4 hr in the temperature range 70 – 130 ^{o}C in the presence of different amounts (10 – 100 mg) of S-MWCNTs as a catalyst a solid brown pasty mass was obtained. The polymeric product isolated from CH_2Cl_2 was found to be different with respect to its appearance and texture, depending on the reaction conditions (table 1). It is noteworthy here that when the reaction was conducted in the presence of pristine MWCNTs, no polymeric product was obtained. It indicated the catalytic role of acid treatment of pristine MWCNTs in the polymerization reaction.

When the amount of the catalyst was 10 mg no polymeric product was obtained irrespective of increase in reaction temperature from 70 – 130 ^{o}C and the duration of the reaction varied from 1 – 4 h. However a significant increase in the isolated yield of the polymeric product was observed with an increase in not only the amount of the catalyst but also duration and temperature of the reaction. This observation indicates the requirement of a minimum amount of acid activated MWCNTs to initiate the polymerization reaction. The raise in the activity with the amount of the catalyst may be attributed to an increase in the number of active centers which are probably the acidic sites. These catalytically active acid sites on the MWCNTs are generated by sulphuric acid treatment. The presence of acid sites in S-MWCNTs and its concentration was confirmed by n-butylamine titration method.

The best yield of the polymer was obtained when the reaction was conducted for 4 h at 110 ^{o}C with 100 mg of the catalyst. The polymeric product under these reaction conditions isolated from CH_2Cl_2 was obtained as off brown solid and its melting point was found to be in the range of 82 – 86 ^{o}C. Further the reusability of the catalyst in the polymerization reaction was evaluated under the same reaction conditions and observed that S-MWCNTs could be recycled up to 5 times without any significant loss in its catalytic activity. Thus this method of synthesis of poly (p-phenylene methylene) is better compared to the protocols already reported in the literature for the same reaction with respect to the

simplicity of the procedure, activity of the catalyst and its non toxic nature
.

TABLE 1: THE CATALYTIC ACTIVITY OF S-MWCNTS IS INVESTIGATED BY USING DIFFERENT AMOUNT OF S-MWCNTS, DURATION AND TEMPERATURE OF THE REACTION IN THE CONVERSION OF BENZYL ALCOHOL IN TO PPM.

Sl. No	Catalyst amount (mg)	Duration of the reaction (hr)	Temperature of the reaction (^{o}C)	Amount of isolated Product (g)	% Yield of the product
1	10	1	70	-	-
		2	90	-	-
		3	110	-	-
		4	130	-	-
2	20	1	70	0.2	5.95
		2	90	0.3	8.92
		3	110	0.5	14.88
		4	130	0.6	17.85
3	40	1	70	0.3	8.92
		2	90	0.4	11.90
		3	110	0.6	17.85
		4	130	0.7	20.83
4	60	1	70	1.2	35.71
		2	90	1.4	40.17
		3	110	1.5	44.04
		4	130	1.7	49.70
5	80	1	70	1.9	55.05
		2	90	2.1	61.90
		3	110	2.9	85.11
		4	130	3.0	89.28
6	100	1	70	2.1	63.09
		2	90	2.5	73.51
		3	110	3.2	93.15
		4	130	3.2	93.15

2) Characterization of Poly (p-phenylene Methylene) (PPM):

The molecular weight of the isolated polymer determined by GPC analysis was found to be 1711g/mol and the number average was 263 g/mol respectively. The polydispersity index value (6.506) of the obtained polymer indicates the presence of non-homogenized monomers with branches. Powder X-ray diffraction pattern of the polymer is given in the fig. 1. Polymer exhibited characteristic diffraction peaks of PPM at 2θ =18.87 and 43.48 indicating low crystallinity of the material. The peak at 2θ =18.87 was broad, indicating partly crystalline nature and lack of π-stacking of the biphenyl groups in the structure [9].
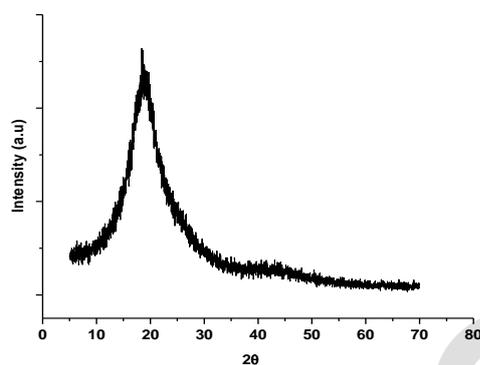
Fig. 1 Powder –XRD patterns of Poly (p-phenylene methylene)

FT-IR spectra of the polymer fig. 2 exhibited bands at 3439 cm^{-1}, 3021cm^{-1} and 2915 cm^{-1} characteristic of O-H, aromatic C-H and – CH$_2$ bond stretching vibrations respectively [13]. Out of the plane indicates (OOPs) vibrations of aromatic C-H bond at 689.48 cm^{-1}. Thus FT-IR spectra analysis indicated the presence of all the characteristic group frequencies of PPM.
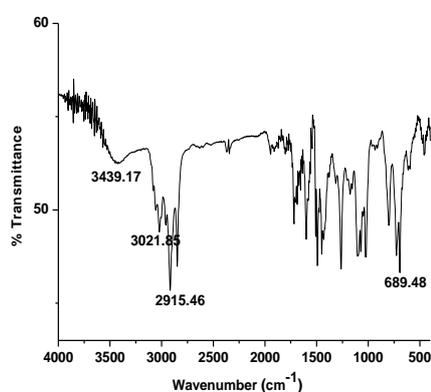
Fig. 2 FT-IR spectra of Poly (p-phenylene methylene)

The structure of the polymer was confirmed by both ^{1}H NMR and ^{13}C NMR analysis. The ^{1}H NMR spectra of the polymer is given in the fig. 3. Polymer showed an intense singlet appearing at 7.1ppm which is associated with aromatic hydrogen. Singlet at 3.8 ppm which is due to methylene proton and also observed the peak at 2.9ppm which is due to hydroxyl hydrogen respectively [9].
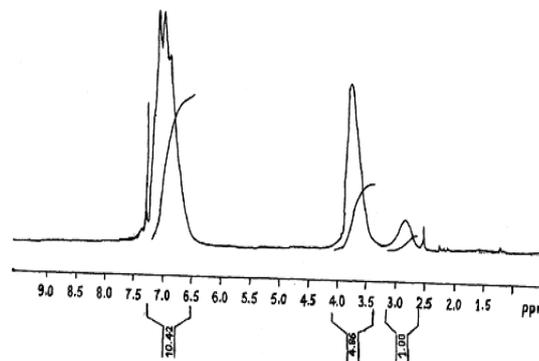
Fig. 3 ^{1}H NMR Spectra of (p-Poly phenylene methylene)

^{13}C NMR spectrum of the polymer shows aromatic carbon signals around 128 ppm and 138 ppm, the later signal is due to the quaternary carbons of the phenyl ring. The aliphatic carbon signals are noticed in the range of 39-41ppm [9] (^{13}C NMR spectrum is given as supplementary data). The highly intense peak at 76 ppm is due to the solvent (CDCl$_3$) used [14].

SEM image of the polymer is given in fig. 4, which indicate that the polymeric material has flakes like morphology.
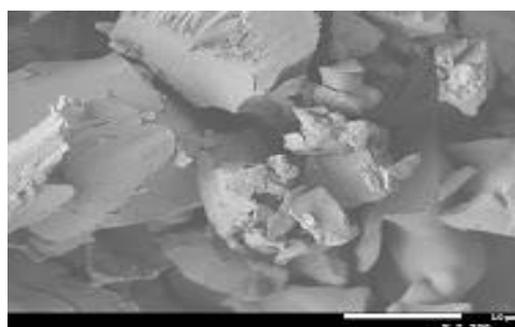
Fig. 4 SEM image of (p-Poly phenylene methylene)

3) Catalyst characterization:

Powder X-ray diffraction patterns of pristine MWCNTs and S-MWCNTs are given in fig. 5. The pristine MWCNTs exhibited a strong symmetrical diffraction peak at 2θ=25° which is characteristic of its graphitic structure. Upon acid treatment the intensity and symmetry of this peak significantly altered, indicating the interaction of the H$_2$SO$_4$ with the graphitic structure of MWCNTs. FT-IR spectra of both pristine and S-

MWCNTs are given as supplementary data. They showed a broad band around 3400cm^{-1} characteristic of stretching vibration of hydroxyl groups. These hydroxyl groups are associated with either strongly adsorbed water molecules and/or the hydroxyl /carboxyl functional groups generated on acid treatment of the MWCNTs [15]. The bands at 1382 cm^{-1} and 1178 cm^{-1} are attributed to asymmetric and symmetrical stretching mode of SO_2 [16]. These studies confirmed the incorporation of sulphate ions from sulphuric acid which contributed to the acidity of S-MWCNTs. The increase in surface acidity of MWCNTs on acid treatment was further confirmed by n-butyl amine method of estimation of acid sites concentration. Surface acidity of pristine MWCNTs and S-MWCNTs were found to be 0.66 and 3.84 m mol/g respectively. This surface acidity of S-MWCNTs is responsible for its catalytic activity in the conversion of Benzyl alcohol to PPM.

BET surface area of S-MWCNTs was found to be 53.64m^2/g, pore volume 0.186 cm^3/g and pore size 139.1 A^o where as for pristine MWCNTs surface area 238.22m^2/g, pore volume 1.67 cm^3/g and pore size 267.94 A^o. This clearly indicates of textural modification that has occurred on treatment of carbon nanotubes upon sulphuric acid treatment. The surface morphology and elemental composition of the MWCNTs was analyzed by SEM and EDS analysis is given in fig. 6. Pristine MWCNTs appears to have a loose porous texture. Upon acid treatment the MWCNTs are agglomerated resulting in a denser texture. The composition of C, O and S as indicated by EDS analysis. This result confirms the incorporation of sulphur species into the structure of MWCNTs upon the respective acid activation.
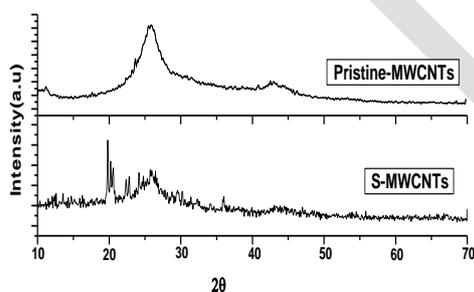
Fig. 5 Powder -XRD patterns of pristine and S-MWCNTs.

Element	Wt %	At %
C K	49.44	61.37
O K	32.39	30.18
S K	18.17	8.45
TOTAL	100	100
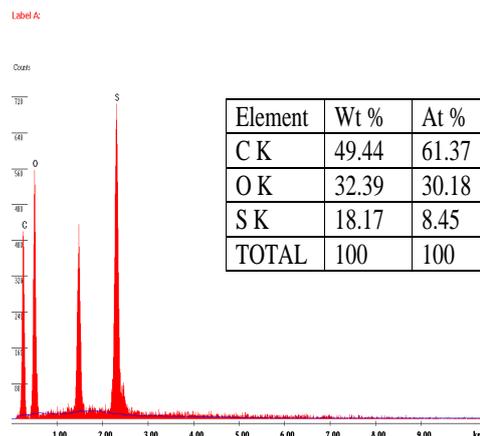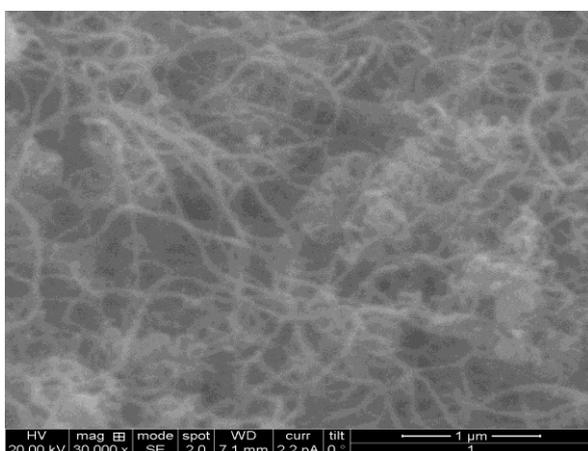
Fig. 6 SEM image and EDS profile of S-MWCNTs.

CONCLUSION

MWCNTs upon treatment with concentrated sulphuric acid followed by sonication, gain surface acidity which has been found to be catalytically active for the synthesis of poly (p-phenylene methylene) polymer from benzyl alcohol. The maximum yield of isolated polymeric product was found to be 93.1%. The catalyst was found to be recyclable up to 5 cycles without any loss in its activity. The method is found to be superior to those already reported in the literature with respect to simple protocol and environmentally benign nature.

ACKNOWLEDGEMENT

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SUPPLEMENTARY DATA
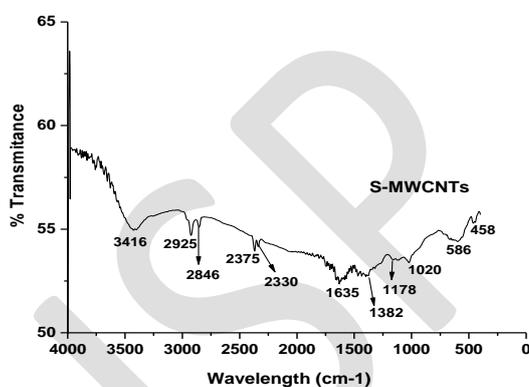
FT-IR Spectra of S-MWCNTs
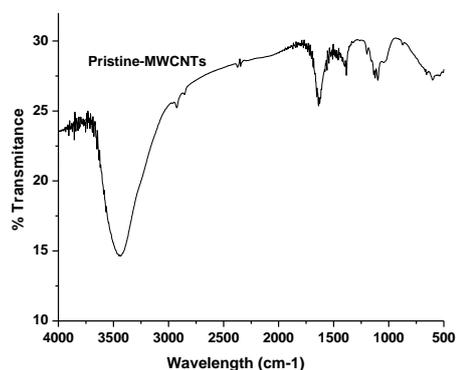
FT-IR Spectra of Pristine MWCNTs

n- butyl amine back titration method

   0.1g of solid catalyst is suspended in 10 cm^3 of benzene solution of 0.05M n-butylamine and the mixture is left for overnight. During this period all the acid sites on the surface of the solid get neutralized. The unreacted butyl amine is estimated by titrating against 0.05M HCl using bromothimol blue as an indicator.
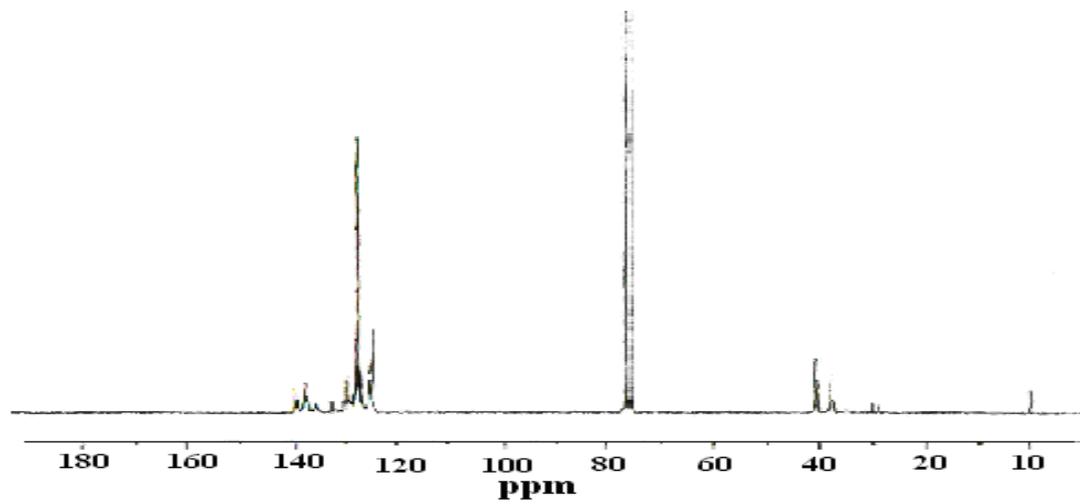
Fig. ^{13}C NMR Spectra of Poly (p-phenylene Methylene)