

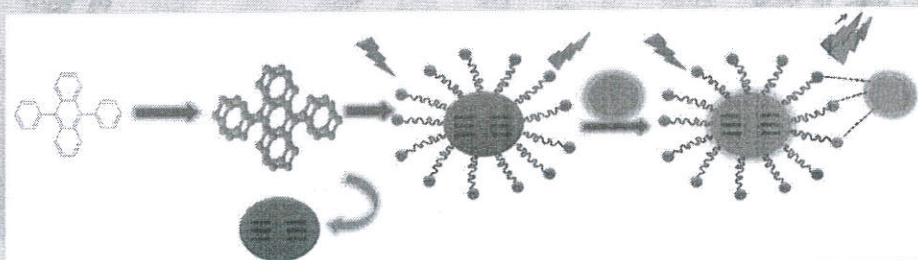


Macromolecular Symposia

392

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Advances in Materials Science – ICAMS 2020 (Part I)



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A Facile Synthesis of Poly(3-octyl thiophene):Ni_{0.4}Sr_{0.6}TiO₃ Hybrid Nanocomposites for Solar Cell Applications

Vinayak Adimule, Anusha Suryavanshi, Yallur BC, Santosh S. Nandi

First Published: 19 August 2020

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Synthesis, Impedance, and Current–Voltage Characteristics of Strontium-Manganese Titanate Hybrid Nanoparticles

Anusha Suryavanshi, Vinayak Adimule, Santosh S. Nandi

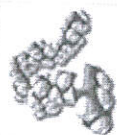
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Synthesis and Characterization of MnS Thin Film at Room Temperature for Supercapacitor Application

Aishwarya Admuthé, Sambhaji S. Kumbhar, Susmita. K. Chougule, Ganesh N. Padasare, Mallikarjun M. Tonape

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AIE Emission of SDS Capped Diphenylanthracene Nanoparticles for Selective Recognition and Estimation of Al³⁺ Ion in Aqueous Medium Based on Enhancement Effect and Analytical Application

Sonali B. Suryawanshi, Gunvant R. Deshmukh, Anita J. Bodake, Shivajirao R. Patil

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✓ Synthesis and Characterization of New Organosoluble and Thermally Stable Aromatic Polyamides Containing Flexible Ether, Ketone, and Methylene Linkages

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Physical and Fourier Transform Infrared Studies of ZnO-Al₂O₃-Li₂O-B₂O₃ Glass System Incorporated with Cu²⁺ and Mn³⁺ Ions



Synthesis and Characterization of New Organosoluble and Thermally Stable Aromatic Polyamides Containing Flexible Ether, Ketone, and Methylene Linkages

Arati Diwate,* Shivaji Ghodake, Asalam Tamboli, Kiran Patil, Mahesh Gurame, and Noormahammad Maldar*

A new aromatic diacid monomer, namely, 1,4-phenylene-bis-[[4'-(4"-carboxy methylene) phenoxy phenyl] methanone] (PBCPPM) is successfully synthesized and characterized by physical constant, FT-IR, NMR (^1H and ^{13}C) spectroscopy, and mass spectrometry. Synthesis of new series of polyamides with high thermal stability and improved solubility are performed by Yamazaki's direct phosphorylative polycondensation method from new PBCPPM with different aromatic diamines. The inherent viscosity of these polyamides is in the range $0.47\text{--}0.81\text{ dL g}^{-1}$. All these polyamides are amorphous or partly crystalline and reveal good solubility in polar aprotic solvents and exhibit glass transition temperatures between 201 and $232\text{ }^\circ\text{C}$. Initial decomposition temperatures are in the range $300\text{--}367\text{ }^\circ\text{C}$ and T_{10} is in the range of $376\text{--}414\text{ }^\circ\text{C}$ indicating good thermal stability of these polyamides. The present observations suggest that these polyamides can find potential applications as high performance polymers.

aromatic polymers greatly enhances molecular mobility and provides better solubility and it may decrease thermal transitions and stability.^[6–8]

Previous results have validated this approach, and work reported in this section is designed to extend new options through the synthesis of a new aromatic diacid containing ether, ketone, and methylene links, namely, 1,4-phenylene-bis-[[4'-(4"-carboxy methylene) phenoxy phenyl] methanone] (PBCPPM), and its polycondensation with different aromatic diamines producing polyamides with enhanced molecular mobility and solubility.

1. Introduction

Aromatic polyamides is an important class of high-performance polymers with repeating amide groups linked to aromatic rings, having excellent balance of mechanical and thermal properties.^[1] Despite their special properties, they have limited application because of their intractability.^[2] In fact, they do not melt but decompose at higher temperatures and can be processed only from solutions in highly polar organic solvents containing inorganic salts. For that reason, great efforts are focused on modifying the chemical structure of these materials. Various attempts were made for improving their processability and, more specifically, their solubility in organic solvents.^[3–5] In this respect, it is found that the introduction of flexible linkages, into the main chain of

2. Results and Discussion

2.1. Synthesis of Diacid Monomer

The diacid, namely, PBCPPM was successfully synthesized from 4-hydroxy phenyl acetic acid and bis 1,4(4'-fluoro benzoyl) (Scheme 1).

2.2. Spectral Characterization

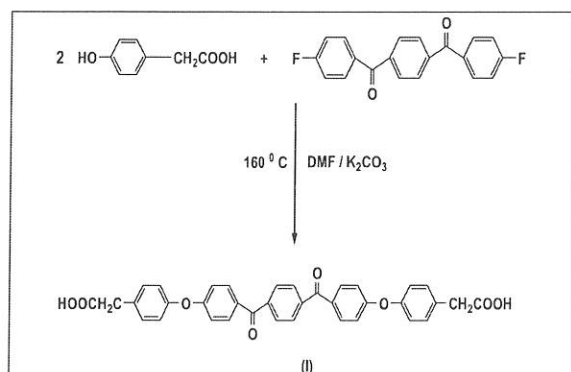
The structure of PBCPPM was confirmed by FT-IR, ^1H and ^{13}C NMR spectroscopy and mass (HRMS) spectrometry. The spectral analysis values are in good agreement with the expected values for the proposed structure.

FT-IR spectrum of PBCPPM (Figure 1) showed characteristic absorption band at 2926.96 cm^{-1} (aliphatic C—H stretching due to the presence of CH_2) and band at 3061.02 cm^{-1} (O—H stretching), 1720.52 cm^{-1} amide II (C=O stretching), and 1224.38 cm^{-1} (C—O bond stretching). Its ^1H NMR spectrum showed a singlet at $\delta\ 3.5$ corresponding to methylene protons whereas doublets due to aromatic protons were observed in the range of $\delta\ 6.96$ to 7.72 (Figure 2). ^{13}C NMR showed a signal at $\delta\ 173.08$ is due to carbonyl carbon of carboxylic acid and a signal at $\delta\ 193.69$ is due to carbonyl carbon (Figure 3), whereas methylene carbon appeared at $\delta\ 40.56$ this was confirmed by DEPT ^{13}C NMR (Figure 4) where in negative peaks of $-\text{CH}_2-$ appeared downside at $\delta\ 40.08$. All

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Scheme 1. Synthesis of 1,4-phenylene bis[[4'-(4''-carboxy methylene phenoxy) phenyl] methanone] (I) (PBCPPM).

aromatic carbons were in the range of δ 117.2 to 161.28 ppm. HRMS spectrum (Figure 6) showed $[M^+]$ peak at m/e 586 and $(M^+ + 1)$ peak at m/e 587 indicating molecular weight of diacid is 586 corresponding to the molecular formula of $C_{36}H_{26}O_8$.

2.3. Synthesis of Polyamides Using Yamazaki's Phosphorylative Direct Polycondensation

A series of new polyamides bearing ether, ketone, and methylene linkage was successfully prepared by polymerization of PBCPPM with different commercial diamines (Scheme 2). Triphenyl phosphite (TPP) was used as the condensing agent, where in the mixture of *N*-methyl-2-pyrrolidone (NMP) and pyridine (4:1 by volume), containing 8 wt% anhydrous lithium chloride, acted as solvent. The polymerization was carried out at 110 °C for 3 h under nitrogen. The resulting polymer was precipitated by pouring the

viscous reaction mixture in excess of methanol. The yields and inherent viscosities of all polyamides are summarized in Table 1.

2.4. Characterization of Polymers

All these polyamides were characterized by different techniques such as solubility, inherent viscosity, FT-IR, differential scanning calorimetry (DSC), thermogravimetry (TGA), and XRD. Solubility tests for all polyamides were determined in different organic solvents with 0.5% polymer concentration. All polyamides showed good solubility in NMP, DMAc, DMSO, DMF, *m*-cresol, and pyridine. Improved solubility character can be attributed to the preformed ether, and methylene group in the polymer backbone. However these polyamides were insoluble in chlorinated solvents like $CHCl_3$, DCM, and acetone and partially soluble in THF, etc. The inherent viscosities of these polyamides were in the range of 0.47–0.81 dL g⁻¹ in NMP indicating moderate to high molecular weight build up. Inherent viscosity of polyamide PFODA based on ODA was high among the series (Table 1). This was attributed to the higher reactivity of ODA.

The formation of the polyamides was confirmed by FT-IR spectra. The representative FT-IR spectrum of polyamide PFSDA is given in Figure 5. All polyamides showed characteristic amide absorption bands at 3228.28 (amide —NH stretching), 1656.36 (amide-I, C = O stretching) and 1588 cm⁻¹ (amide-II, —NH deformation).

Proper knowledge of the thermal stability of polymers is essential for appropriate applications of polymers. The thermal properties of these polyamides were evaluated by DSC and thermogravimetry. The DSC curves of all polyamides are shown in Figure 7, whereas TGA curves are shown in Figure 8. Table 2 incorporates the thermal data. The polyamides had glass transition temperatures in the narrow range of 185–222 °C. This close range of T_g s probably indicates that the T_g s of these polyamides

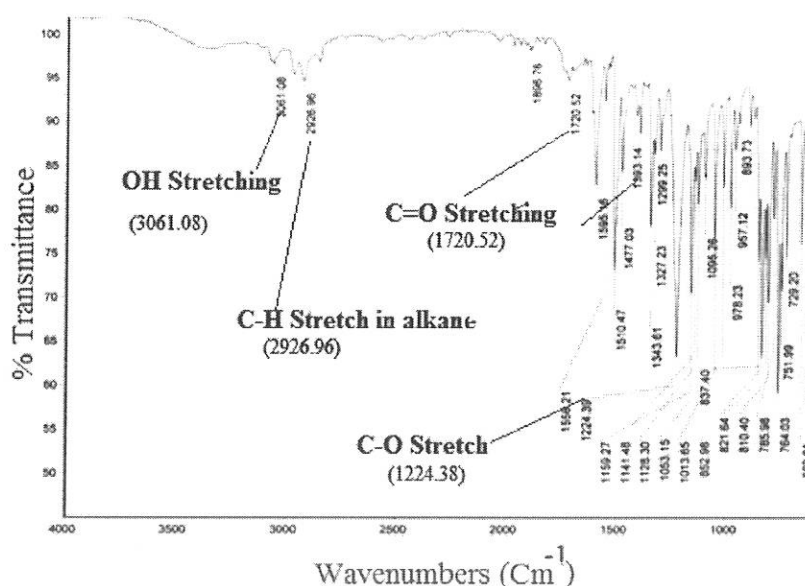
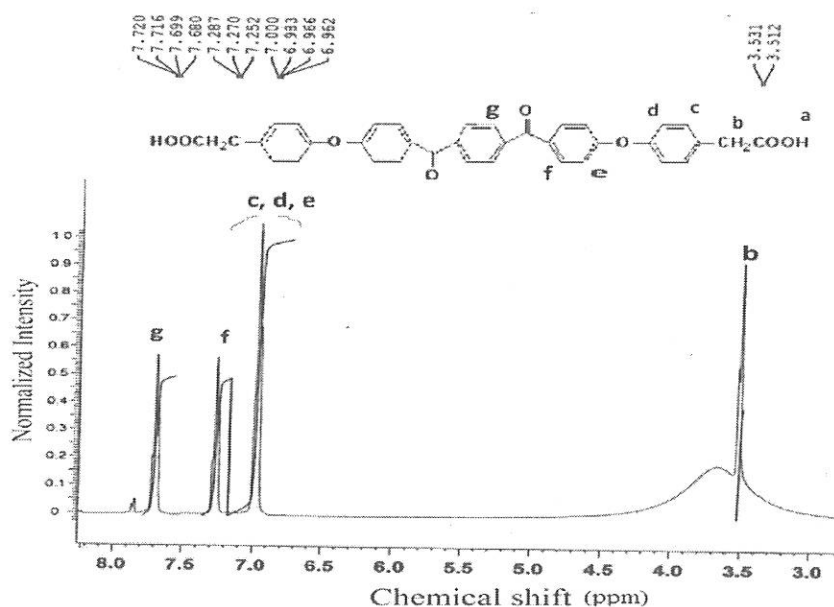
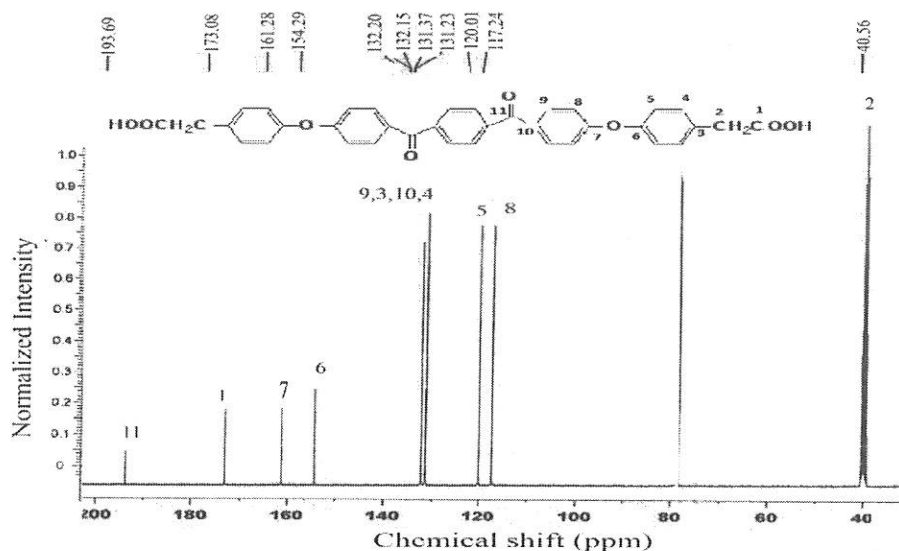


Figure 1. FT-IR spectrum of (PBCPPM).

Figure 2. ^1H NMR spectrum of PBCPPM in d_6 -DMSO.Figure 3. ^{13}C NMR spectrum of PBCPPM in d_6 -DMSO.

were mainly dependent on diacid structure and had no major contribution from aromatic diamine units.

The thermal stability of polyamides was investigated by TGA to evaluate the degradation pattern via weight loss. All these polyamides showed a similar pattern of decomposition with no weight loss below 300 °C (T_i 300 to 367 °C). The polymers showed T_{10} values were in the range 376–414 °C and the char yields at 800 °C were in the range 55%–62% indicating the high thermal stability of polyamides. This showed that the introduction of ether, ketone, and methylene flexible linkages in polymer backbone improved solubility without much effect on thermal stability polyamides.

A broad diffraction peaks of diffused type centered at 20° (2θ) are observed in X-ray plots. As indicated in Figure 9, these polymers show similar diffraction patterns typical of amorphous materials with two polyamides indicating shoulder at end. Thus polymers were largely amorphous in nature and supported the solubility behavior of these polyamides.

3. Conclusions

The aromatic diacid containing flexible ether, ketone, and methylene linkages; 1,4-phenylene bis[4'-(4"-carboxy methylene

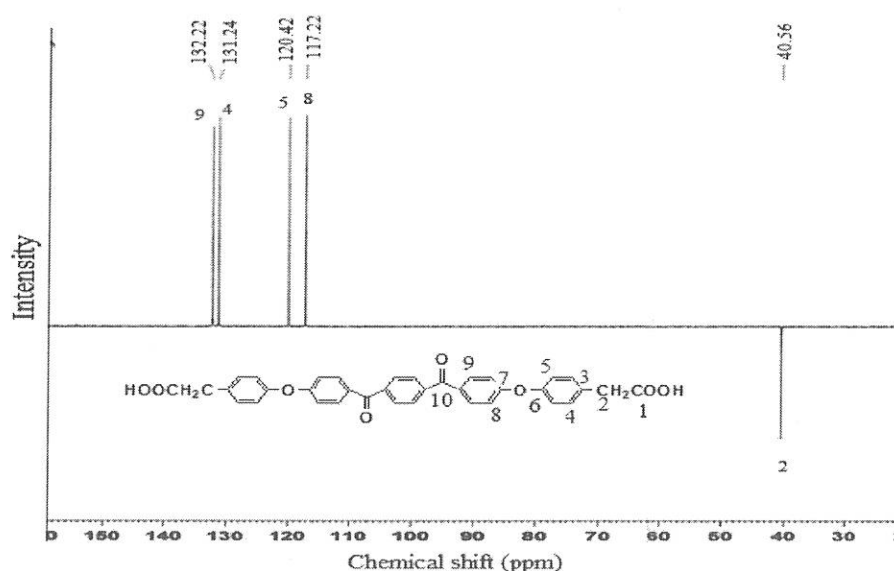
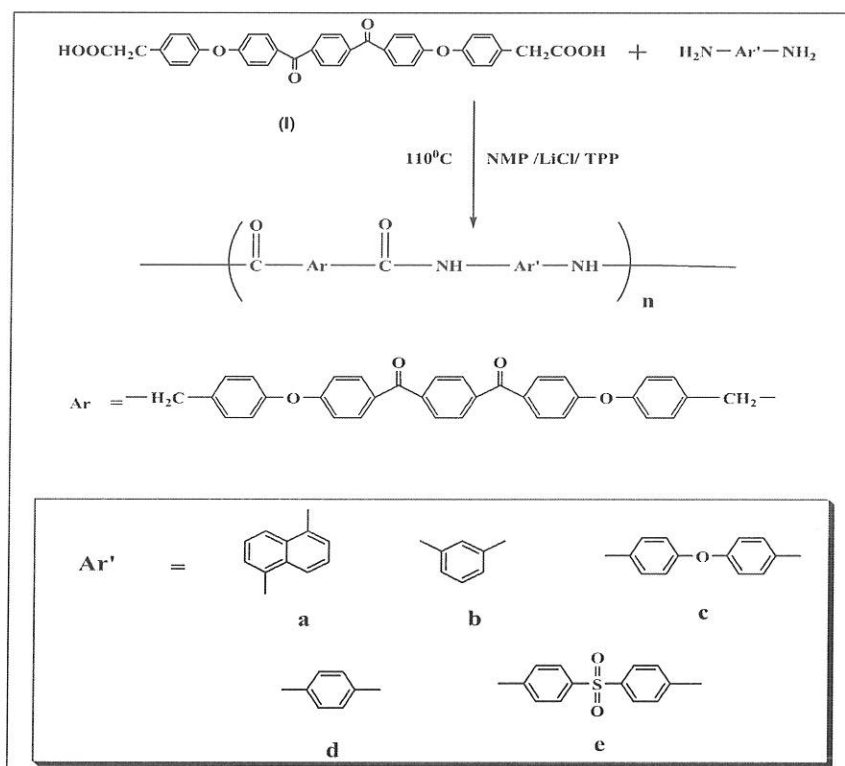


Figure 4. DEPT¹³C NMR spectrum of PBCPPM in d₆-DMSO.



Scheme 2. Synthesis of polyamides from 1,4-phenylene bis[[4'-(4''-carboxy methylene phenoxy) phenyl] methanone] (I) by Yamazaki phosphorylative direct polycondensation method.

phenoxy) phenyl] methanone] (VI) was synthesized successfully and characterized by physical constant, FT-IR, ¹H NMR, ¹³C NMR, DEPT¹³C NMR, and mass spectrometry. Using Yamazaki's phosphorylation method, polyamides were prepared from new aromatic diacid of 1,4-phenylene bis[[4'-(4''-carboxy methy-

lene phenoxy) phenyl] methanone] (VI) and various aromatic diamines in NMP solution containing LiCl using triphenylphosphite and pyridine as condensing agents. Inherent viscosity values of polyamides were in the range 0.47–0.81 dL g^{−1} indicating built up of moderate to high molecular weight polymers.

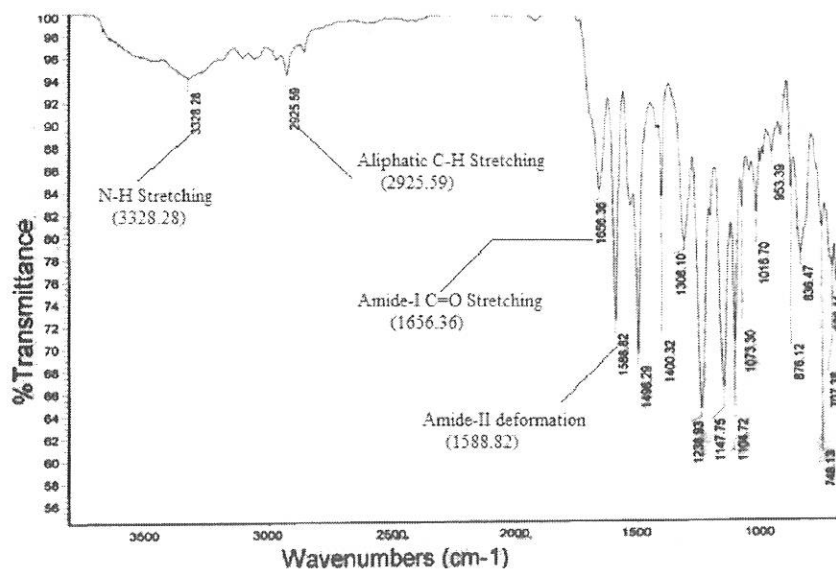


Figure 5. FT-IR spectrum of polyamide PFSDA.

Table 1. Yield, inherent viscosity of polyamides from PBCPPM.

Serial no.	Polymer code	Diacid	Diamines	Yield [%]	η_{inh} [dL g ⁻¹]
1.	PFNDA	PBCPPM	1,5-naphthalene diamine	98.6	0.78
2.	PFMPDA	PBCPPM	m-phenylenediamine	98.8	0.61
3.	PFODA	PBCPPM	Oxy dianiline	99.0	0.81
4.	PFPDA	PBCPPM	p-phenylenediamine	98.1	0.67
5.	PFSDA	PBCPPM	Sulphonyldianiline	98.5	0.47

The incorporation of flexible methylene linkages and thermally stable ether and ketone groups which are also flexible into the backbone of these polymers remarkably enhanced the solubility while maintaining good thermal stability. Therefore, these new polyamides which are processable, are good candidates for use in various in high-performance applications.

4. Experimental Section

Materials: 4-Hydroxy phenyl acetic acid, bis-1,4(4-fluoro benzoyl) benzene and triphenyl phosphate were purchased from Aldrich and used as received. Anhydrous K₂CO₃ was dried in vacuum at 150 °C for 6–8 h. NMP was distilled under reduced pressure. Pyridine was refluxed over KOH pellets, distilled, and stored over 4 Å molecular sieves.

Measurements: Viscosity measurements were carried out with a 0.5% (w/v) polymer solution in NMP at 30 °C with an Ubbelohde suspended level viscometer. ¹H NMR spectra were recorded on a Bruker AV-III 400 MHz instrument (the reference was 0 ppm with tetramethylsilane (¹H)). An FT-IR spectrum was recorded with a Thermo Nicolet IS 10 FT-IR spectrometer. DSC measurements were made on a Mettler Toledo instrument at a heating-cooling rate of 10 °C min⁻¹ under nitrogen. The *T_g* was taken at the middle of the step transition in the second heating run. TGA was measured on a Mettler Toledo instrument. A heating rate of 10 °C min⁻¹ was used for the determination of the decomposition temperature

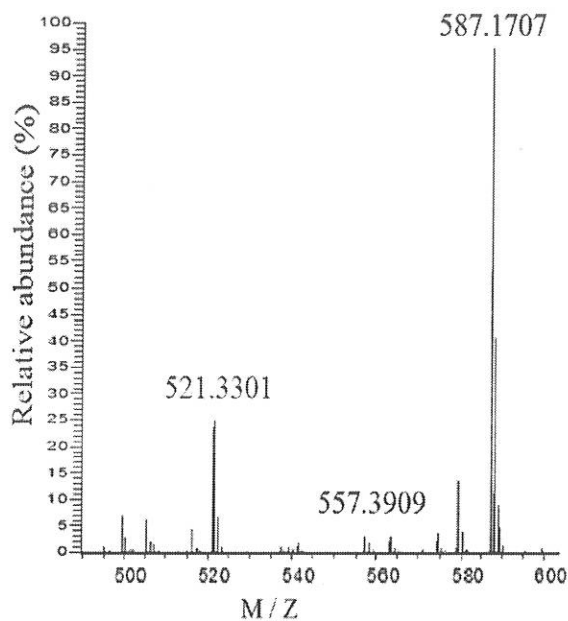


Figure 6. Mass spectrum of PBCPPM.

at a 10% weight loss under nitrogen gas. X-ray diffraction pattern was obtained on Ultima IV X-ray diffractometer.

Synthesis of Diacid Monomer (1,4-Phenylene bis[4-(4-carboxy methylene phenoxy) phenyl] methanone): A 500 three neck round bottom flask equipped with a water condenser, a calcium chloride guard tube, a magnetic stirrer, a nitrogen gas inlet, and a thermowell was flame dried under the flow of nitrogen gas. 4-hydroxy phenyl acetic acid 4.56 g (0.03 mol), bis 1,4(4'-fluoro benzoyl) benzene 4.85 g (0.015 mol), and anhydrous K₂CO₃ 2.76 g (0.02 mol) were charged in it. NMP 60 was added to it and the reaction mixture was stirred at 150–160 °C for 14 h. The mixture was

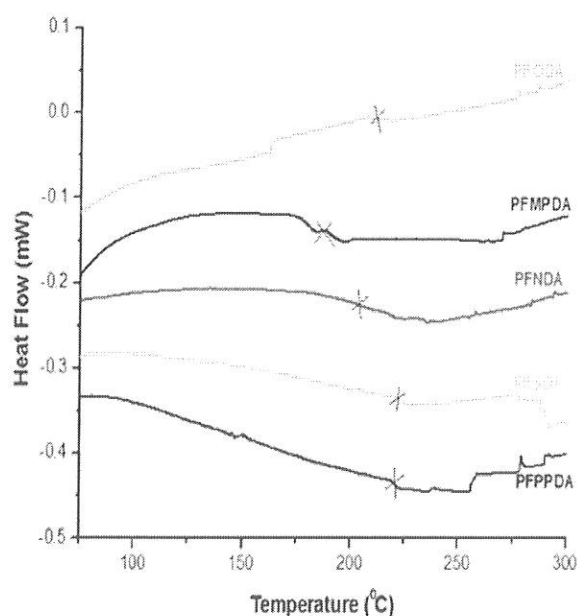


Figure 7. DSC curves of polyamides.

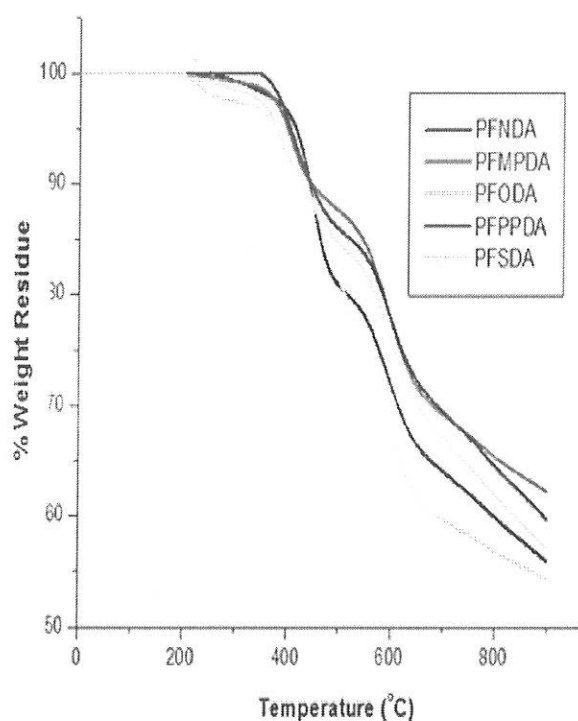


Figure 8. TGA of polyamides from PBCPPM.

cooled to room temperature and poured into water (200) to precipitate a yellow product which was collected by filtration, washed with hot water, and dried. The product was purified by recrystallization from CH_3OH . The yield of purified product was 6.32 g (72%). M.P. = 202 °C, M.W. = 586 g. FT-IR ν cm^{-1} was 1686.32, 2917.86, 1342.73, 1596.67, 1498, 1244.76, and 801 cm^{-1} . ^1H NMR (DMSO- d_6 , 400 MHz) δ was 6.96 to 7.72 (d, Ar-H), 3.5 (S, 4H) ppm, and ^{13}C NMR (DMSO- d_6 , 400 MHz) δ 40.56, 154.29, 161.28,

Table 2. Thermal properties of polyamides from PBCPPM.

Polymer code	Temperature for various % decomposition [°C]			Char yield [%] at 800 °C	T_g [°C]
	T_1	T_5	T_{10}		
PFMDA	319	399	445	59	200
PFMPDA	315	414	442	65	185
PFODA	305	378	431	61	213
PFPPDA	367	404	444	64	220
PFSDA	300	376	428	56	222

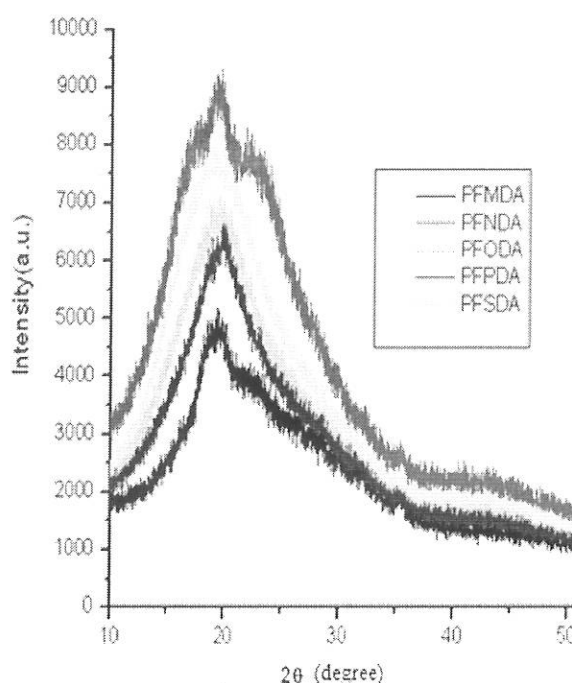


Figure 9. XRD of polyamides.

131.15, 131.37, 117.22, 120.02, 131.22, 131.24, 173.08, and δ 193.69. ppm. DEPT ^{13}C NMR (DMSO- d_6 , 400 MHz) a downside peak at δ 40.56 and up-side peaks at, δ 117.22, δ 120.02, δ 131.22, and δ 131.24 ppm. HRMS m/e 587 [M^+].

Polymer Synthesis: The reaction pathway leading to the synthesis of polyamides is shown in Scheme 2. In a 100 three neck round bottom flask equipped with a reflux condenser, a magnetic stirrer, a calcium chloride guard tube, and a nitrogen gas inlet were placed 0.2 g (1 mmol) ODA, 0.2 g lithium chloride [8 wt% based on solvent NMP and pyridine mixture] and 0.744 g (0.63, 2.4 mmol) TPP, 0.5 pyridine and 3 mL NMP, and 0.586 g (1 mmol) (PBCPPM). The reaction mixture was stirred well and temperature was slowly raised to 100 °C over a period of 30 min. and the temperature was maintained at 110 °C for 3 h. After cooling the resultant viscous solution was poured into rapidly stirred methanol 200. The precipitated polymer (PFODA) was filtered, washed with methanol, and dried under vacuum at 100 °C for 8 h. The yield was 99.0% and the inherent viscosity of was 0.81 dL g^{-1} . All the polyamides were prepared similarly.



Conflict of Interest

The authors declare no conflict of interest.

Keywords

diacid, ether, polyamides, solubility, thermally stable

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