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Synthesis and Characterization of New Polyesters Using Schiff Base Monomer

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Two new polyesters were synthesized *via* polycondensation using Schiff base monomer, 2,3-*bis*[(4-hydroxybenzylidene)amino]maleonitrile with sebacoyl chloride and terephthaloyl chloride. Both the monomer and polyesters were characterized by FT-IR and ^{1}H NMR. The solubility of the polyesters was examined with various solvents. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index were determined by gel permeation chromatography. The DSC curves were obtained from differential scanning calorimeter in a dynamic nitrogen atmosphere.

Keywords: Polyester, Schiff base, Polycondensation.

INTRODUCTION

Polyester is a class of polymer which has diversified applications in industrial sectors. Polyester with entity of conjugated (–C=C-) and (–C=N-) bonds (Schiff base), in their main chain unit have created an interest among the researchers due to their importance in many aspects [1-3]. Schiff base bonds (-C=N-) confers appropriate features to the polyester material such as conductivity, liquid crystal properties, thermal stability and chelating effects [4,5]. Aromatic polymers with Schiff base units (–C=N-) have high thermal stability and low solubility which restrict their applications [6]. To address this problem, much researches have been done on increasing the solubility [7,8]. Substituting pliable groups along the main chain of polyesters with Schiff base units is one of the approaches to enhance the solubility in organic solvents [9]. We have synthesized high molecular weight polyesters using Schiff base monomer as main unit with dihalogen compounds *viz.*, sebacoyl chloride and terephthaloyl chloride. The resulting polyesters have high thermal stability and solubility.

EXPERIMENTAL

Synthesis of monomer: Schiff base monomer of 2,3-*bis*-[(4-hydroxybenzylidene)amino]maleonitrile (PAB-2NS) was obtained by condensing 4-hydroxy benzaldehyde with 2,3-diaminomaleonitrile in ethanol and few drops of hydrochloric acid were added to the flask. The mixture was stirred for 5 h under reflux condition. After cooling the reaction, the precipitated monomer was purified by washing with ethanol and dried in a vacuum oven at 70 °C for 3 h. An orange solid was obtained in 76 % yield and the melting point was found to be 233 °C.

Synthesis of polyesters: Polycondensation was carried out by **Scheme-I** by adding a DMF solution of sebacoyl chloride or terephthaloyl chloride to a suspension of an equimolar amount of Schiff base monomer in presence of triethylamine at 0 °C. The resulting mixture was stirred for 4 h at room temperature. The reaction mixture gradually became homogeneous during the polymerization and the reaction was terminated with water. Final product was obtained as a brown solid for both the polyesters and it was purified by washing with methanol followed by aqueous solution of sodium bicarbonate and dried under reduced pressure at 80 °C for 24 h.

RESULTS AND DISCUSSION

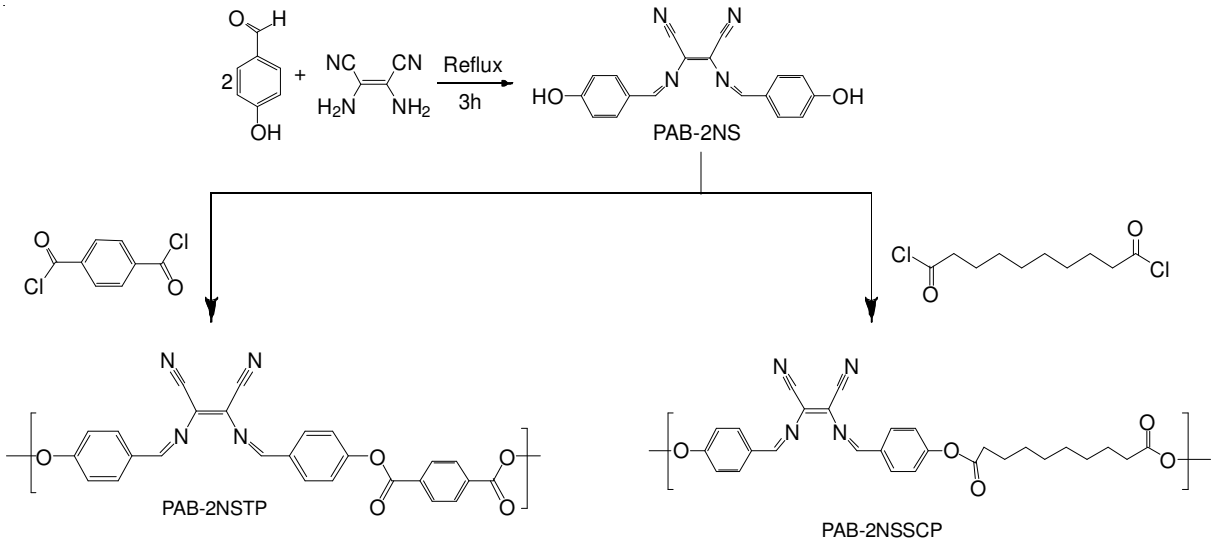
Spectral data of monomers

IR spectra: The band at 3205 cm^{-1} is assigned to OH group. The absorption peak at 3122 cm^{-1} is for (NH) group. The stretching frequency of nitrile group (C≡N) appears at 2222 cm^{-1} while that of imine group (C=N) appears at 1659 cm^{-1}. The absorption peak at 1590 cm^{-1} is characteristic of double bond (C=C$_{Ar}$) (Fig. 1a).

^{1}H NMR spectrum: The peak at 9.15 ppm is characteristics of OH proton and the peak at 8.38 ppm is assigned to C*H*=N. The peaks at 8.01 ppm and 7.01 ppm are characteristic of aromatic region (Ar*H*).

Spectral data of polyesters

IR spectra of two polyesters PAB-2NSTP and PAB-2NSSCP: The bands at 1730 and 1749 cm^{-1} are assigned to



Scheme-I

carbonyl stretching (C=O), the peaks at 1677 and 1652 cm^{-1} are attributed to (C=N) and the peaks at 1490 and 1493 cm^{-1} are related to double bond stretch (C=C), respectively (Fig. 1b and 1c).

^{1}H NMR spectra of the polyesters: Signal at 8.40 ppm is due to the proton of azomethine, the peak in the region 6.09-8.01 ppm is related to the protons of aromatic groups. The peaks due to protons of methyl group appear at 1.09-2.8 ppm.

Solubility of polyesters: The solubility characteristics of the polyesters are shown in Table-1. It is observed that both polyesters are insoluble in chloroform and toluene and soluble

TABLE-1
SOLUBILITY BEHAVIOUR OF POLYESTER

Compounds	Solvent				
	DMF	DMSO	THF	$CHCl_3$	Toluene
PAB-2NSSCP	++	++	++	–	–
PAB-2NSTP	++	++	++	–	–

Solubility: ++ Soluble at room temperature; – insoluble

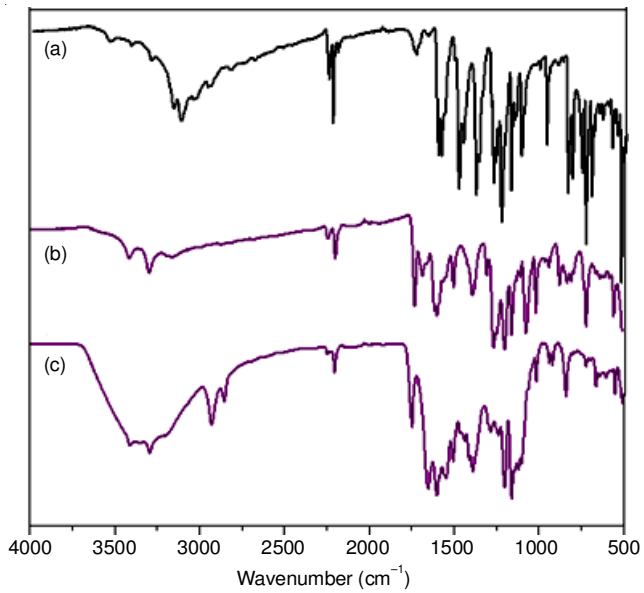


Fig. 1. FT-IR spectra of (a) PAB-2NS, (b) PAB-2NSTP, (c) PAB-2NSSCP

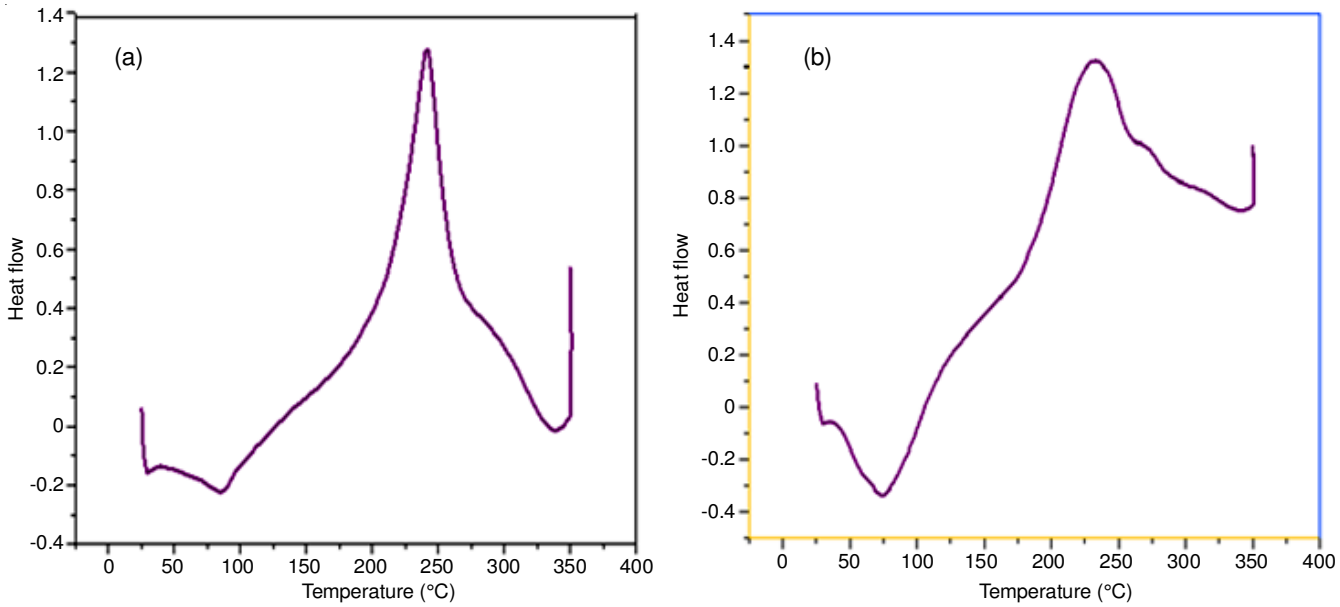


Fig. 2. DSC thermogram of (a) PAB-2NSTP, (b) PAB-2NSSCP

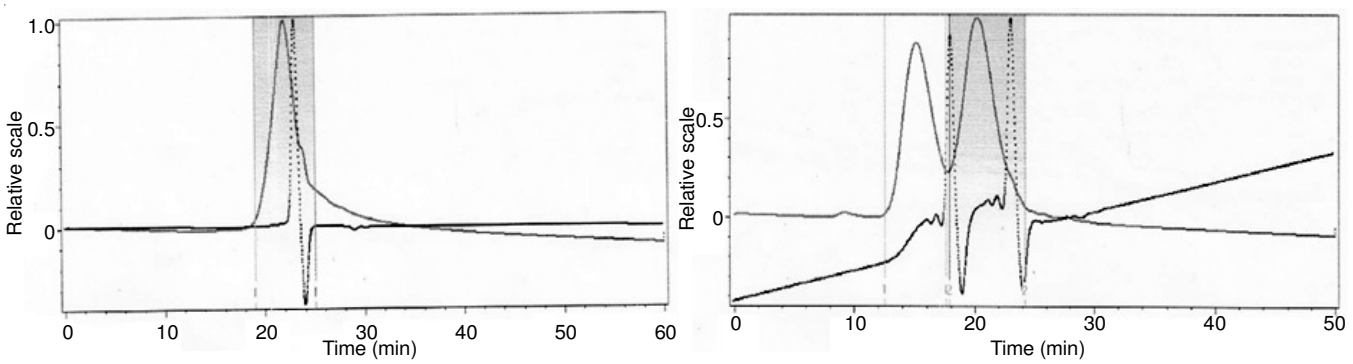


Fig. 3. GPC chromatogram of the synthesized polyester

in dimethyl formamide, dimethyl sulphoxide and tetrahydrofuran.

Thermal stability of polyester was investigated by differential scanning calorimeter at a heating rate of 10 °C/min. DSC traces of the synthesized polyesters (PAB-2NSTP and PAB-2NSSCP) are given in Fig. 2. The glass transition temperature (T_g) of polyester varies in the range of 332.66-393.17 °C. This value could be attributed to the stability of polyesters which depends on the structure of the long chain aromatic and aliphatic ester groups.

The GPC chromatogram of the synthesized polyester is shown in Fig. 3. The number average molecular weight (M_n) and weight average molecular weight (M_w) of both polyesters can be calculated and M_n ranges from 95000 to 100000 units. The values of polydispersity index (PDI) of 0.167 and 0.184 mL/g (Table-2) show that the distribution is extremely broad for both the polyesters.

TABLE-2
NUMBER AVERAGE MOLECULAR WEIGHT (M_n), WEIGHT AVERAGE MOLECULAR WEIGHT (M_w), POLYDISPERSITY INDEX (PDI) OF THE SYNTHESIZED POLYESTERS

Compounds	M_n (g/mol)	M_w (g/mol)	PDI	dn/dc (mL/g)
PAB-2NSTP	2.454×10^4	1.1×10^5	4.525	0.1679
PAB-2NSSCP	1.561×10^3	6.7×10^4	4.339	0.184

Surface morphology is studied by the synthesized Schiff base polymers (Fig. 4). The size ranges from 500 to 10 µm for the both the polyesters is observed with flatter surfaces particles and non-routine cracks and gaps.

Conclusion

In summary, two new polyesters prepared from Schiff base monomer have polydispersity index distribution extremely broad and both the polyester have high molecular weight and moderate solubility in various solvent. The polyesters have glass transition temperatures in the range 332.66-393.17 which shows that the polyesters are thermally stable. For future studies, Schiff base monomers containing chromone moiety will also be used as an alternative to the existing diols which may find applications in pharmacological studies.

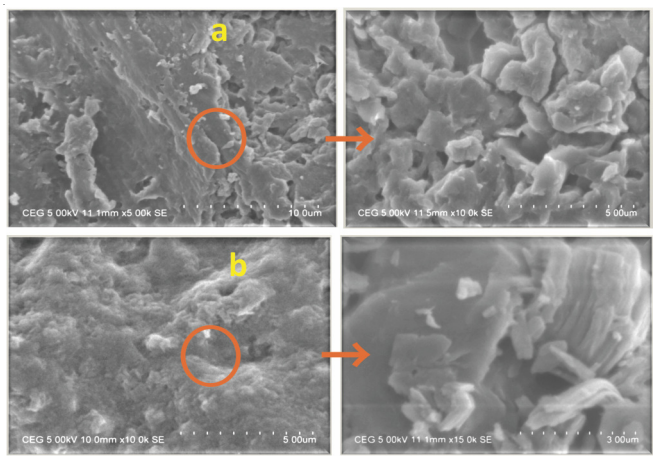


Fig. 4. SEM photographs of (a) PAB-2NSTP, (b) PAB-2NSSCP

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