

SYNTHESIS AND CHARACTERIZATION OF CERTAIN THERMOTROPIC RANDOM COPOLYESTERS

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ABSTRACT

A new category of poly(ester-amide)s based on diarylidene cyclohexanone in the main chain were synthesized via interfacial polycondensation of monomers namely: bis(4-hydroxybenzylidene) cyclohexanone, Resorcinol and Hydroquinone as diols with diacid chlorides and characterized. The inherent viscosities of the resulting polyesters were in the range of 0.1- 1.4 dl/g. These polyesters were characterized by H^1 NMR, C^{13} NMR, IR, UV – Visible Spectroscopy and DSC. These polyesters have wide application such as drug carriers, agricultural films, matrix resins for biomedical materials and biological water treatment. The synthesized poly(ester-amide)s also found to have photocrosslinkability with biomedical application.

Keywords: Copolyesters, bis (4-hydroxybenzylidene)cyclohexanone, Resorcinol, Quinol

INTRODUCTION

The importance of thermotropic random copolyester has been recognized and several workers have reported the synthesis and characterization of various copolyester which exhibit different mesophase in the melt. Calundann [1] reported the liquid crystalline copolyester compositions based on hydroxy benzoic acid, hydroquinone, 2,6 naphthalene diol, and 4,4'-biphenol and also granted a patent for this preparation. Liquid crystalline polyesters have positional and orientational molecular order which is intermediate between that of molecular crystals and of liquids. The liquid crystalline polyesters do not melt directly to a liquid phase, but first pass through a mesomorphic state, which at a higher temperature forms a clear liquid. The moieties which generate the liquid crystalline organization are called the mesogenic moieties and can be found either in main or side groups. Polymers which exhibit liquid crystalline nature in solution are termed as lyotropic and those that exhibit in melt are called thermotropic [2]. The structural characteristics associated with liquid crystalline behavior have been reviewed by Gray[3]. Several thermotropic highly aromatic liquid crystalline polyesters such as Vectra and Xydar have been commercialized. These polyesters are thermally stable and possess high tensile strength and modulus. The application of liquid crystal polymers are in the area of fibres, films, plastics, holography, photocrosslinkages and as information storage devices.

MATERIALS AND METHODS

1,2 dichlorobenzene(Ranbaxy LR), Resorcinol(Loba),Hydroquinone(Loba), bis(4-hydroxybenzylidene) cyclohexanone(Prepared sample),Succinoyl chloride (Sigma Aldrich). Analar samples of $CHCl_3$, DMSO, DMF, Methanol, ether is used as such.

POLYMER SYNTHESIS

Preparation of Random Copolyester PBRS

A 250ml three necked round bottomed flask equipped with a mechanical stirrer, a nitrogen inlet, a reflux condenser and a thermometer was used. To the flask added O-dichlorobenzene(150ml), then added Resorcinol 1.1g(0.01 mole) followed by bis(4-hydroxybenzylidene) cyclohexanone 3.06g(0.01 mole). The

mixture was stirred for 20 minutes and temperature was gradually increased to 120°C. To this reaction mixture, added succinoyl chloride 2.25ml (0.02mole). Then the whole mixture was maintained with further stirring and heating at 120°C-140°C for 12-14 hours. The reaction mixture was poured into n hexane with stirring to precipitate the polymer. The precipitated polymer was separated by filtration, recrystallized by dissolving in acetone and poured in water, filtered and then dried. The copolyester was obtained as a pale brown solid.

Preparation of Random Copolyester PBQS

This Random Copolyester was prepared by the similar procedure with Hydroquinone 1.10g (0.01mole), bis(4-hydroxybenzylidene) cyclohexanone 3.06g (0.01mole) and Succinoyl chloride 2.25ml (0.02mole). The polymer was obtained as dark brown solid.

Polymer Characterisation

IR spectra for the dried polymer samples were recorded in IFS66V FT-IR spectrometer, in KBr pellets containing powdered polymer.

The ¹H NMR spectra were recorded using JEOL GSX 400 FT-NMR spectrometer operating at room temperature 24°C. Samples for analysis were prepared by dissolving about 10mg of the copolyester in 5ml of spectral grade DMSO solvent.

DSC analysis of the polyester PBRS and PBQS was carried out in (1.1) netzsch DSC unit. The experiment were done in nitrogen atmosphere at a heating rate of 2°C/min. About 5mg of powdered sample was used with close packing.

The UV-Visible spectra of these polyesters were recorded in Shimadzu-uv-160A spectrophotometer using ethanol as solvent.

The inherent viscosities of these polymers were determined in o-chlorophenol using Ubbelonde viscometer at 30°C

RESULTS AND DISCUSSION

1. VISCOSITY

The inherent viscosity of random copolyester PBRS in o-chlorophenol was found to be 0.08064dL/g at 30°C.

The inherent viscosity of random copolyester PBQS in o-chlorophenol was found to be 1.4041dL/g at 30°C.

The inherent viscosity of PBQS is higher than that of PBRS. This shows that para oriented polymer have higher viscosity than meta oriented polymer. This may be due to the fact that m-orientation of benzene ring reduce the rigidity and hence the effective volume.

2. IR spectrum

The strong absorption band at 1757cm⁻¹ indicates the presence of ester carbonyl groups. The strong bands at 1016 cm⁻¹, 1125 cm⁻¹, 1162 cm⁻¹ is due to the carbonyl stretching of ester group. The three bands at 2931 cm⁻¹, 801 cm⁻¹ and 835cm⁻¹ are due to -CH₂- stretching and bending vibration. The absorption band at 1600cm⁻¹ is due to the arylidene keto group present in copolyester.

The IR spectrum of PBRS and PBQS is almost similar and shown in fig 1 and 3.

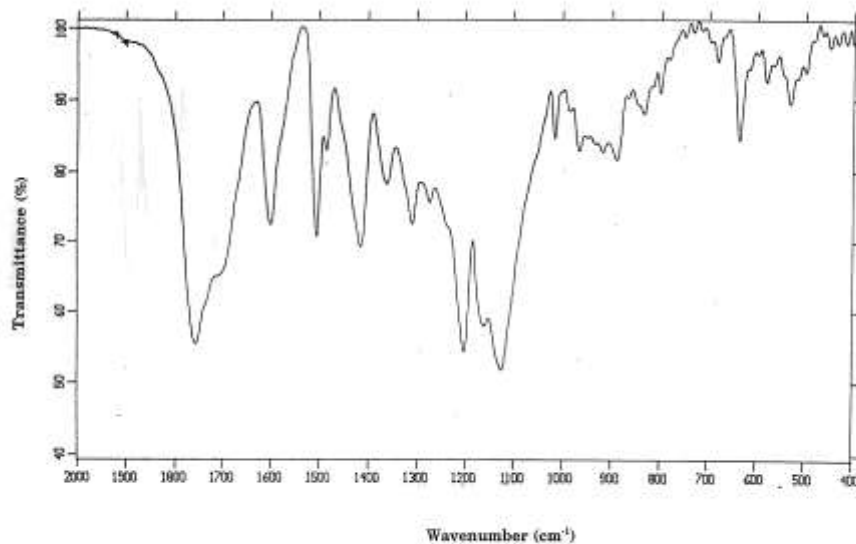


Fig.1 Infrared Spectrum of the Random Copolyester PBRS

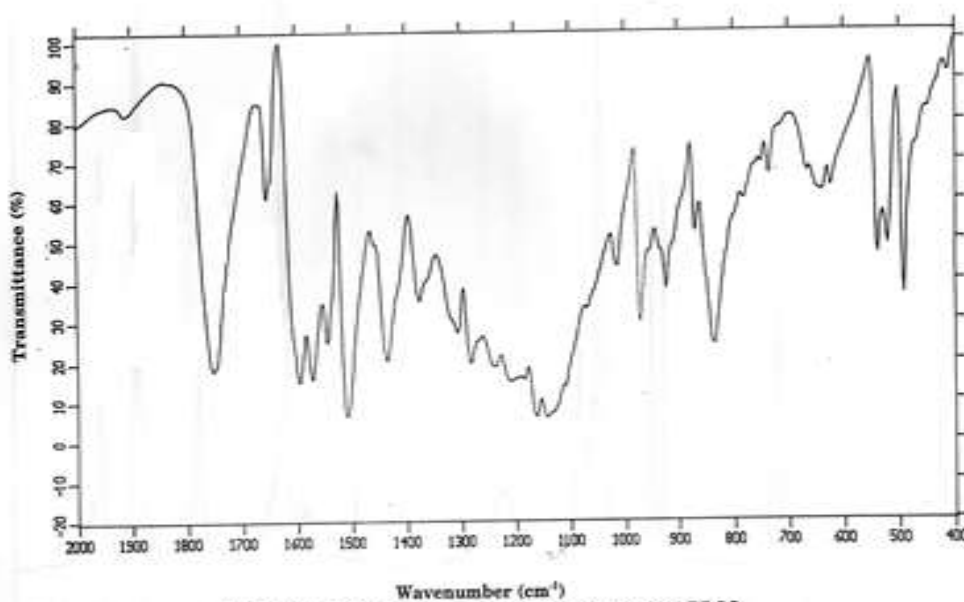


Fig.3 Infrared Spectrum of the Random Copolyester PBQS

3. ^1H NMR spectrum

Protons of cyclohexanone show absorption between 2-3 ppm. The protons of 1,3-phenylene rings present in polymer chain absorb at downfield i.e. between 7-7.4 ppm. The polyester contains methylene groups which absorb at 1.8 ppm.

The ^1H NMR spectrum of PBRS and PBQS is almost similar and shown in fig 2 and 4.

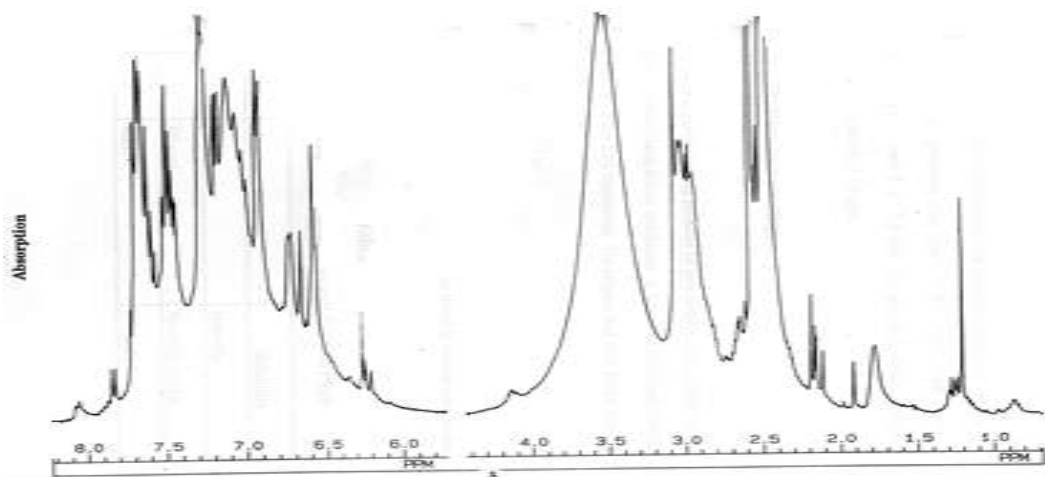


Fig.2 ¹H NMR Spectrum of the Random Copolyester PBRS

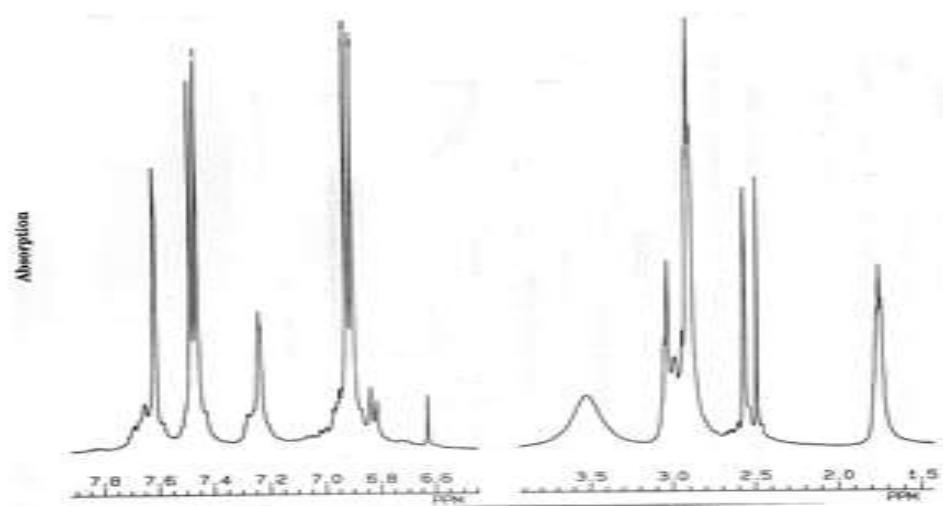


Fig.4 ¹H NMR Spectrum of the Random Copolyester PBQS

4. DSC

DSC thermograms of the two polyesters are given in fig 5 and 6. It is summarized in the following table.

Thermal Properties of Copolyesters

Polymer	(Transition Temperature°C)		
	T _g	T _m	T _{cl}
PBRS	68	191	254
PBQS	89	262	417

PBRS is stable upto 254°C whereas PBQS is stable upto 417°C. This suggests that the polyester containing quinol has greater thermal stability than the polymer with resorcinol group. This may be due to higher molecular mass of PBQS which is supported by viscosity values.

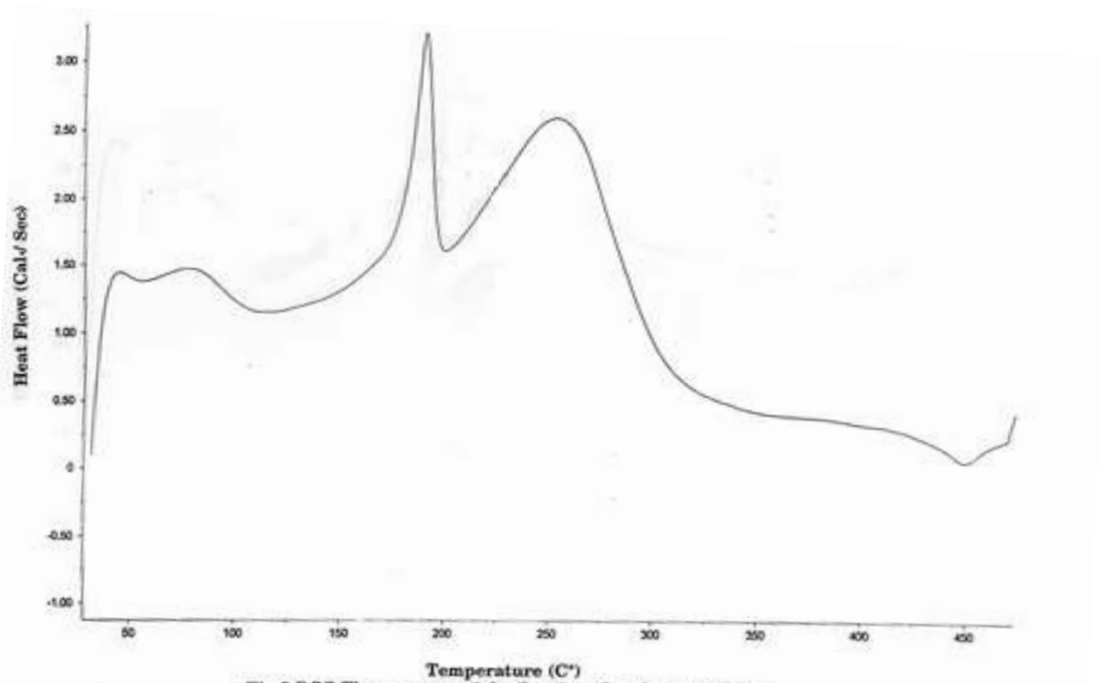


Fig.5 DSC Thermogram of the Random Copolyester PBRS

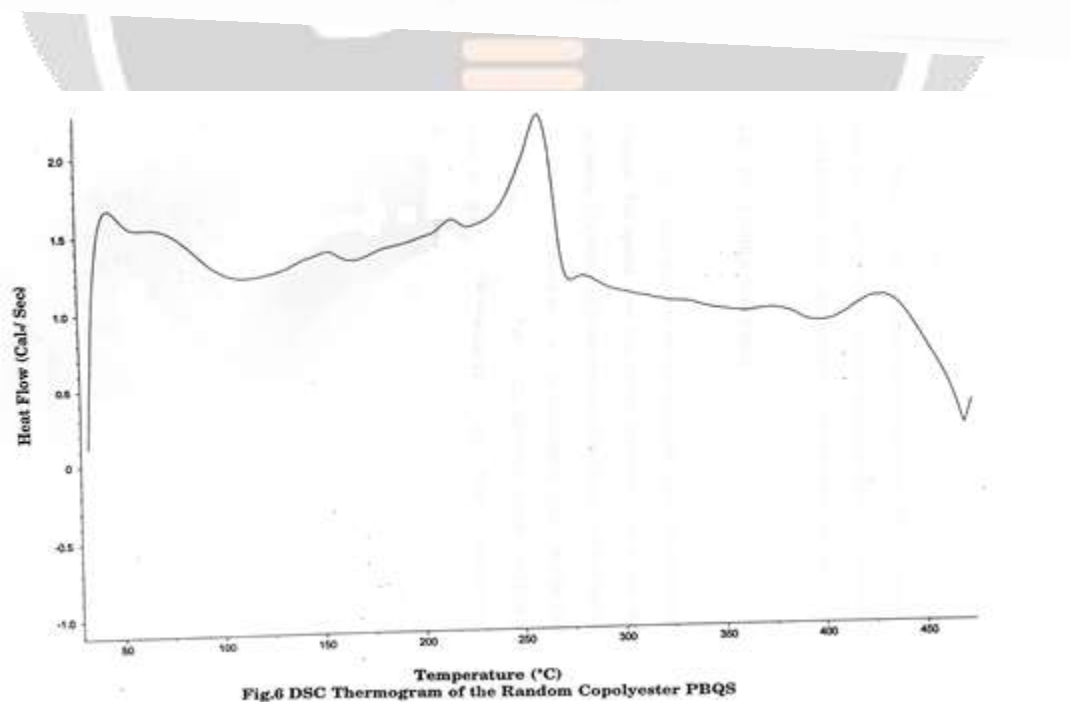


Fig.6 DSC Thermogram of the Random Copolyester PBQS

5. UV – VISIBLE Spectrum

The UV –Visible spectrum of PBQS show a high intensity band around 550nm, which is due to $n-\pi^*$ transitions of carbonyl group and is shown in fig 7.

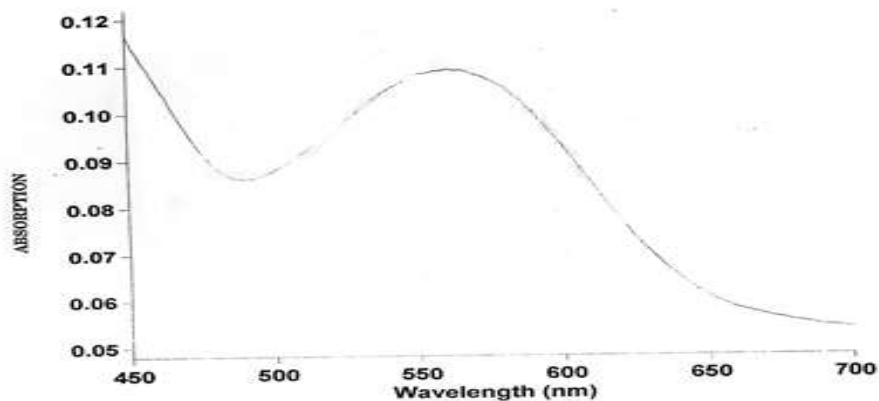


Fig.7 UV - Visible Spectrum of the Random Copolyester PBQS

CONCLUSION

The inherent viscosity of PBQS is greater than PBRS which indicates that PBQS may have high molecular weight than PBRS.

The IR and UV – Visible spectra of the Copolyesters were recorded and interpreted. The absorptions indicated the formation of Copolyesters.

The ^1H NMR spectra of these Copolyesters were recorded. The chemical shifts were explained on the basis of structural units present in Copolyesters.

DSC thermograms show that PBQS has greater thermal stability than PBRS.

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