

Synthesis and Characterisation of Two Random Copolyesters by Phase-Transfer-Catalysed Polycondensation

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Abstract - Polyesters containing chalcone moiety were synthesised from 1, 3-bis (4-hydroxy-3-methoxyphenyl) propanone (BHMPP) and 1- (3, 5-dihydroxyphenyl)-3-(4-methoxyphenyl) propanone (DHPMPP) with suberoyl and sebacoyl chlorides by an interfacial polycondensation technique. Fundamental studies on the two phase polycondensation using phase transfer catalyst (tetra n-butylammonium bromide) was done. The synthesised polymers were characterised by solubility measurement, intrinsic viscosity, IR, ¹H and ¹³C NMR studies.

Intex Terms - Copolyesters; spectral studies; phase-transfer catalyst; polycondensation

1 INTRODUCTION

The family of polyesters comprises all polymers with ester functional groups in the polymer back bone [1]. In principle, the synthesis of polyesters or esters in the presence of large amount of water has only been studied by a few research groups. Saam et al. studied the polycondensation in suspension of hydrophobic diol and diacid compounds using different sulfonate surfactants [2-4]. They defined the principles of such polycondensation and showed that polyesters of low molecular weight could be obtained in aqueous media. More recently, Manabe et al. studied the esterification of hydrophobic mono-functional compounds in aqueous suspension [5-7]. Copolyesters, obtained from a multiplicity of reactions having the component groups linked in a random or statistical order, are termed random copolyesters. They retain their strength, clarity and other mechanical properties, despite being exposed to a variety of chemicals that typically affect other materials, such as polycarbonates. This includes their

versatility and flexibility which enhances their application effectively in the design of high-volume, low cast parts as well as critical, more expensive component parts.

Phase transfer catalysis is a synthetic technique which involves transport of an organic or inorganic salt from a solid or aqueous phase into an organic/liquid phase where reaction with an organic soluble substrate takes place. Chalcones are 1, 3-diphenyl-2-propene-1-one, in which two aromatic rings are linked by a three carbon α , β -unsaturated carbonyl system. They possess conjugated double bonds and a completely delocalised π -electron system on both benzene rings [8]. Molecules possessing such system have relatively low redox potentials and have a greater probability of undergoing electron transfer reactions. Most of the research studies involved only the polymers with side chain chalcone units. There are only few reports on soluble polymers with chalcone units in the main chain. Incorporation of flexible aliphatic chain segments into the polymer backbone improves the solubility. The present work deals with the synthesis and characterisation of polyesters containing chalcone chromophore in the main chain and study of their properties.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

Adipic acid (Ranbaxy), sebacic acid (SDS) and thionyl chloride (SDS) were purchased and used [9]. 4-hydroxy benzaldehyde (Merck), 4-hydroxy-3-methoxy benzaldehyde

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(Merck) were used as received. Tetra-n-butylammonium bromide (TBABr, Fluka) was purchased and used. Spectral grade DMSO-d₆ (Aldrich) containing TMS as internal standard was used as received for recording NMR spectra.

2.2 Synthesis of monomer

2.2.1 1,3-bis (4-hydroxy-3-methoxyphenyl) prop-2-en-1-one (BHMPP)

A mixture of 4-hydroxy-3-methoxy benzaldehyde and 4-hydroxy-3-methoxy acetophenone kept dissolved in methanol. The reaction was allowed to proceed for an hour and then poured into ice cold water the yellow precipitate of BHMPP was filtered, dried and further recrystallised from methanol. Yield: 90%, m.p.: 200°C. FT IR (KBr): 3400 cm⁻¹(ν_{OH}); 1591 cm⁻¹(ν_{C=C}); 1641 cm⁻¹(ν_{C=O}). ¹H NMR (DMSO-d₆): 7.1-8.2δ (aromatic), 9.7 δ (s, 2H, -OH), 3.6 δ (s, 3H, -OCH₃). ¹³C NMR (DMSO-d₆): 188.51 δ (>C=O), 158.24 δ (C-OH), 55.63 δ (-OCH₃). Molecular formula: C₁₇H₁₆O₅, MS (EI) m/z 300[M⁺].

2.2.2 1, 3-bis (4-hydroxy-3-methoxyphenyl) prop-2-en-1-one (BHMPP)

1-(3, 5 -dihydroxyphenyl)-3-(4-methoxyphenyl) propenone was prepared from 3, 5-dihydroxy acetophenone and 4-methoxy benzaldehyde kept dissolved in methanol. The reaction was allowed to proceed for an hour and then poured into ice cold water the yellow precipitate of BHMPP was filtered, dried and further recrystallised from methanol.

2.3 Synthesis of copolyesters

Equimolar quantities of BHMPP (1 mmole) and DHPMPP (1 mmole) were dissolved in 25 mL of aqueous sodium hydroxide (0.1 N) solution and taken in a round-bottomed flask (100 mL). After 15 minutes a solution of 2 mL of 2% phase-transfer catalyst was added and stirred. The mixture was stirred continuously at room temperature for 30 minutes in inert atmosphere. About 25 mL solution of suberoyl chloride (2 mmole) in dichloromethane (DCM) was added. The mixture was maintained at room temperature with continuous stirring for seven hours. The reaction mixture was poured into 100 mL of n-hexane when the solid copolyester was obtained. It was then filtered in vacuum. The crude sample was purified and used. Copolyester PBHR2 was prepared by a similar method using sebacoyl chloride [10, 11]. The scheme is presented below. The aliphatic acid chlorides used in the scheme are given in Table 1.

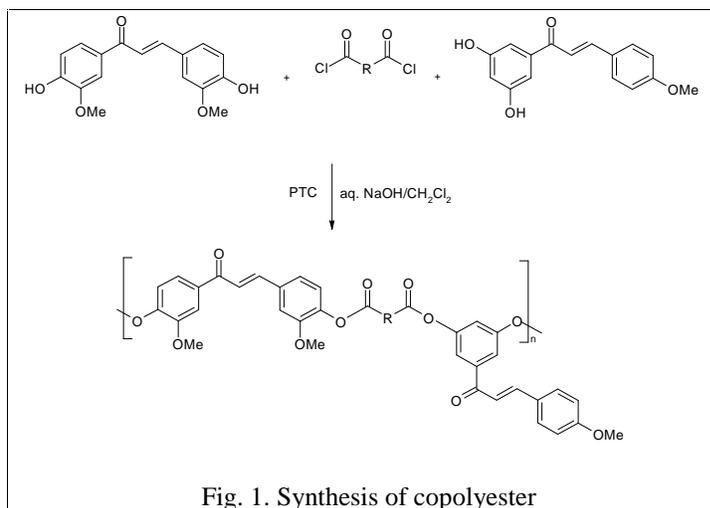


Fig. 1. Synthesis of copolyester

TABLE 1
ALIPHATIC ACID CHLORIDES USED
AND THE COPOLYESTER CODE OF THE FOUR
POLYESTERS

S.No.	Codes of polyesters	Acid chloride (R)
1	PBHR1	-(CH ₂) ₆ -
2	PBHR2	-(CH ₂) ₈ -

3 RESULTS AND DISCUSSION

The synthesised polyesters were characterised by solubility studies, inherent viscosity measurements and spectral studies.

3.1 Solubility

All the synthesised polymers were easily soluble in aprotic polar solvents like tetrahydrofuran, dimethyl sulphoxide, dimethyl formamide, dimethylacetamide, dioxane, and p-cresol and in chlorinated solvents such as methylene dichloride, chloroform and insoluble in toluene, n-hexane, benzene, xylene, diethyl ether and other hydrocarbons solvents. This may be due to the inter-molecular interactions of polar solvents with ester linkage of the polymer molecules. Some of the polymers do not dissolve in the above said solvents; which polymer does not dissolve, in which other solvent is it dissolving. This might be due to the high rigid aromatic nature of the polymers [12, 13].

3.2 Viscosity measurement

The inherent viscosity of the resulting polymers was determined in dimethyl sulphoxide solution at 30°C using Ubbelohde viscometer. In each case, 25 mg of dry pure copolyester sample was dissolved in 25 ml of DMSO, kept aside for some time with occasional shaking. The η_{inh} was

calculated from the flow time measurement. The inherent viscosity values of all the copolyesters are listed in Table 2. The data reveals that these polymers are of reasonably high molecular weight.

TABLE 2
PERCENTAGE OF YIELD AND INHERENT
VISCOSITIES (η_{inh}) OF THE COPOLYESTERS

S.No	Copolyester	Yield (%)	Inherent viscosity (dL/g)
1	PBHR1	78	0.36
2	PBHR2	80	0.38

3.3 Spectral studies

3.3.1 IR spectra

The IR spectrum of PBHR1 is shown in Fig. 2. It exhibits absorption at 1757 cm^{-1} due to carbonyl stretching of the ester group. The peak at 1652 cm^{-1} is due to α, β unsaturated carbonyl stretching. The stretching frequency of trans olefinic double bond is observed at 1505 cm^{-1} and aliphatic C-C stretching gives peak at 1457 cm^{-1} . The absorption band at 1120 cm^{-1} is due to stretching frequency of pendant methoxy group [14]. The peak at 981 cm^{-1} is due to trans configuration of olefinic double bond. The peak at 719 cm^{-1} is due to C-H bending vibrations of benzene nuclei.

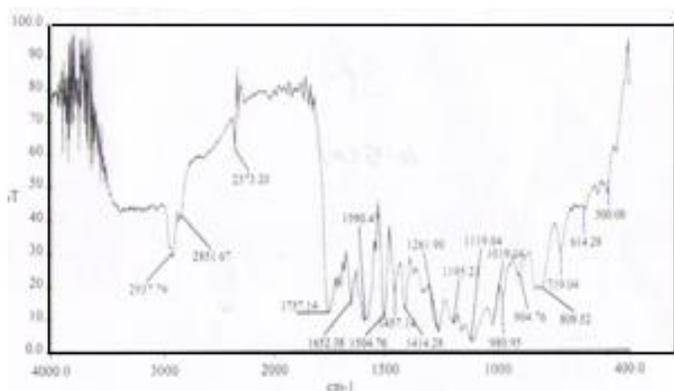
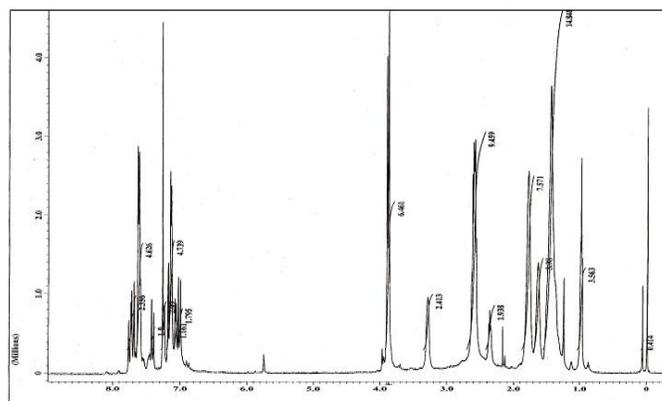


Fig. 2. FT-IR spectrum of PBHR1

3.3.2 ^1H NMR spectra

The ^1H NMR spectrum of PBHR1 is shown in Fig. 3. The aromatic protons of chalcones show multiplet resonance signal between 8.2 and 7.1 ppm. The signal at 6.9 ppm (d) may be attributed to Vinylic protons of chalcone moiety. The resonance signals of the pendant methoxy substituent are observed at 3.3-3.9 ppm. The backbone of aliphatic protons of methylene spacer appear at 0.9-2.7 ppm (m).



δ (ppm)
Fig. 3. ^1H NMR spectrum of PBHR1

3.3.3 ^{13}C NMR spectra

The proton-decoupled ^{13}C NMR spectrum of PBHR1 is shown in Fig. 4. Chemical shift assignments were made from the off-resonance decoupled spectra of the copolymers. The ketone carbonyl carbon and ester carbonyl carbon resonance is observed at 187 and 172 ppm, respectively [15]. The resonance signal at 130 ppm arises from other aromatic carbons in the polymer unit. The Olefinic carbons of vinylic double bond is observed at 122 ppm. The methoxy carbon resonances is observed at about 56 ppm. The aliphatic carbons of the methylene spacers are observed between 21 and 30 ppm.

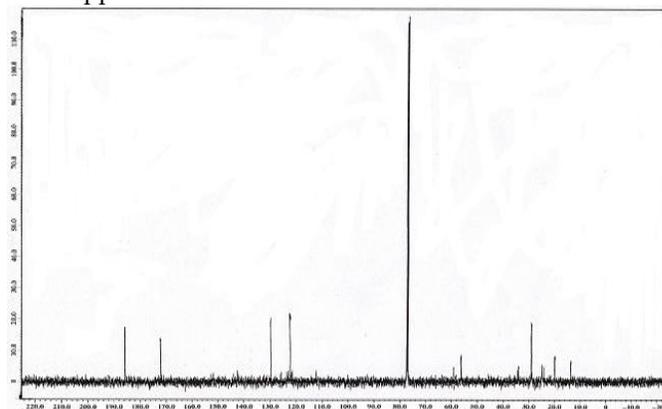


Fig. 4. Proton decoupled ^{13}C NMR spectrum of PBHR1

4 CONCLUSION

Two copolyesters were synthesised using diols 1,3-bis-4-hydroxyl 3-methoxyphenyl propenone (BHMPP) and 1-(3,5-dihydroxyphenyl)-3-(4-methoxyphenyl) propenone (DHPMPP) coupled with aliphatic acid chlorides like

suberoyl and sebacoyl chloride by interfacial polycondensation method by using n-butylammonium bromide as phase transfer catalyst. The copolyesters were characterised by solubility studies, viscosity measurements and spectral studies.

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