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# SYNTHESIS AND CHARACTERIZATION OF POLY {1, 3-BIS [4-(OXY-3-METHOXY) PHENYL]-PROPENONESUBERATE-Co-[(2, 6-BIS (4-OXY-BENZYLIDENE) CYCLOHEXANONE]-SUBERATE}

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**Abstract:**

*In this paper, we report on synthesis and characterization of certain co-polyesters from, 4-hydroxy 3-methoxy propenone4-hydroxy 3-methoxy benzaldehyde by using interfacial polycondensation method. The synthesized random copolyesters characterised by means of* $^{1}$*H NMR,* $^{13}$*C NMR and FTIR. The effect on structural units on the physical properties such as thermal and mechanical properties were invesigaed. Thermal stability was studied by Differential scanning calorimetry (DSC), for polyesters and their blends.*

**Key Words**: Aliphatic-Aromatic Copolyesters, Melt Polycondensation & Thermal Stability.

## 1. Introduction:

Polyester is stretchable and is a category of polymers that contain the ester functional group in their main chain.The formation of polyester is expected to be successful in miniemulsion in order to obtain stable polyester latexes, even though it is not yet reported in the literature. 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[1-5]. The advantages of PTC are inexpensive, non-toxic, readily available chemicals and solvents are recoverable, mild reaction conditions with low energy requirements, enhanced rates of reactions involving anions in non-polar media, increased product specificity, control over reaction conditions and increase the reaction rates and yields. They are cationic and have enough organic moiety so that the catalyst and the desired anion are substantially partitioned into organic phase and aqueous phase. The organic structure is sufficiently large so that the steric hindrance around the cation is more and the cation-anion bonding is close enough to allow high anion reactivity. Types of Phase Transfer Catalysts are quaternary ammonium, phosphonium and arsonium ions, $R_4N^+ X^-$, $R_4P^+ X^-$ and $R_4As^+ X^-$ where R is usually alkyl or benzyl and X refers to different anions in the catalysts and Macrocyclic (crown) (Penderson, 1967) and Macrocyclic (Cryptates) (Dietrich and Lahn, 1973) ethers. The principle of phase transfer catalysis is brought forth well by Reuben and Sjoberg (1981).

The principle of PTC is based on the ability of certain "phase-transfer agents" (the PT catalysts) to facilitate the transport of one reagent from one phase into another (immiscible) phase wherein the other reagent exists. Phase Transfer Catalysis creates selective and efficient conditions for performing a number of polycondensation reactions with attributes of mild conditions and simplicity.

The main objectives of PTC method are to find out the efficiency of the phase transfer catalyst, degree of polymerisation, the role of reactive groups and reactive nature of polymers which have been synthesised and their applications mainly biological effects and antitumor activity[6, 7].

Thus, the present work, deals with the synthesis, characterisation and biological activity of certain random copolyesters which would be copolymerised from a newly synthesised chalcone diol along with two other aromatic diols, four aliphatic diacid chlorides and two aromatic acid chlorides. The catalyst subsequently returns to the aqueous phase and the cycle continues [8-11]. An over view of PTC reactions is given in the scheme below:

## 2. Experimental Details:

### 2.1 Materials:

Methanol (Merck, AR) was refluxed over quicklime for six hours and distilled (b.pt. 65°C). Ethanol (Ranchem, AR) was purified by same method. Chloroform (Merck, AR) was distilled and the middle fraction (b.pt. 173°C) was collected and used. n-Hexane (Merck, AR and b.pt. 40°C) were distilled and used. Merck, AR samples of dimethyl sulphoxide, dimethyl formamide, tetrahydrofuran were purified by distillation before use. Merk sample of cyclohexanone was also used. Spectral grade $CDCl_3$ and DMSO d6 were used for recording NMR ($^1H$ and $^{13}C$) spectra of the copolyesters. Adipic acid (Ranbaxy), sebacic acid (SDS), suberic acid (Fluka), azeleic acid (Merck) and thionyl chloride (SDS) were used. 4-hydroxybenzaldehydes (Merck), 4-hydroxy-3-methoxy benzaldehyde (Merck) were used. Tetra-n-butylammonium bromide (TBABr, Fluka) was purchased and used as such.

### 2.2 Monomer Synthesis:

#### 2.2.1. 1, 3-bis (4-hydroxy-3-methoxyphenyl) prop-2-enone (BHMPP)

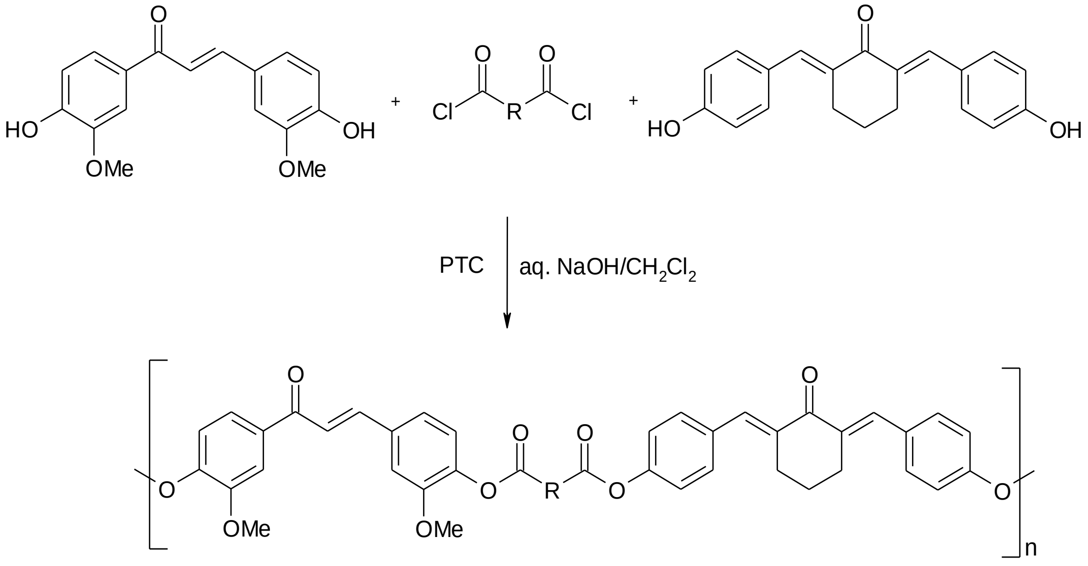
To a mixture of 4-hydroxy-3-methoxy benzaldehyde and 4-hydroxy-3-methoxy acetophenone kept dissolved in dry methanol. The reaction was allowed to proceed for an hour and then poured into ice cold water, the yellow precipitate of BHMPP formed was filtered. It was then filtered and recrystallised from methanol. Yield 90%: IR (KBr): 1657 $cm^{-1}$ ($\nu_{C=O}$), 1601 $cm^{-1}$ (($\nu_{C=C}$) 1072 $cm^{-1}$ ($\nu_{C\text{-}O\text{-}C}$). $^{13}C$-NMR (DMSO-d6): 188.51 δ (>C=O), 158.24 δ and 162 δ (C–OH), 55.8 δ ($-OCH_3$), 16.03 δ($-CH_2$). Mass spectroscopy: m/z value = 301.06.

#### 2.2.2 Polymerisation Procedure:

Equimolar mixture of BHMPP (1 mmole) and BHBCH (1mmole) was dissolved in NaOH solution containing 2mL of 2% TBABr. This mixture was stirred continuously in nitrogen atmosphere. To this mixture, suberoyl chloride (2 mmole) dissolved in DCM was added with vigorous stirring at normal temperature. After some time, the polymer was formed as solid between organic and aqueous layer and was separated and dried in vaccum. The crude sample of PBHCH1 was purified by dissolving in DCM and reprecipitating in n-hexane.

## 3. Results and Discussion:

The monomer 1, 3-bis (4-hydroxy-3-methoxyphenyl) propenone was prepared by condensing 4-hydoxy-3-methoxy acetophenone and 4-hydroxy-3-methoxy benzaldehyde. The polymer was obtained with good yield by interfacial polycondensation method using TBABr as a phase transfer catalyst.



Scheme 1: Synthesis of polymer $P_1$

## 3.1 Spectral Characterization:

### 3.1.1 IR Spectroscopy:

The FT-IR spectra of polymers show absorption bands around 1657 $cm^{-1}$ corresponding to carbonyl stretching vibrations. The polymer PTBHC1 show absorption at 1747.6 $cm^{-1}$, characteristic peak of >C=O stretching vibrations of the ester group which is absent in the IR spectrum of the monomer. The aromatic >C=C< stretching vibration appeared between 1504.7 and 1409.5 $cm^{-1}$. The C-H stretching of –CH2- groups[15, 16] of aliphatic polyester is observed at 2928.2 $cm^{-1}$. The representative FT-IR spectra of polymer P1 is shown in figure 1.

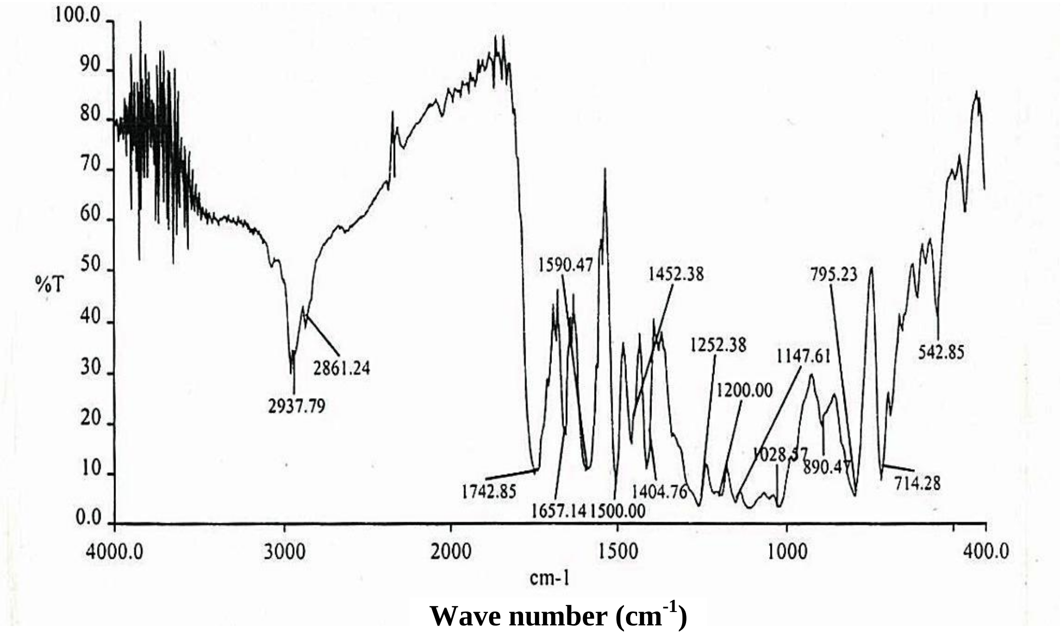
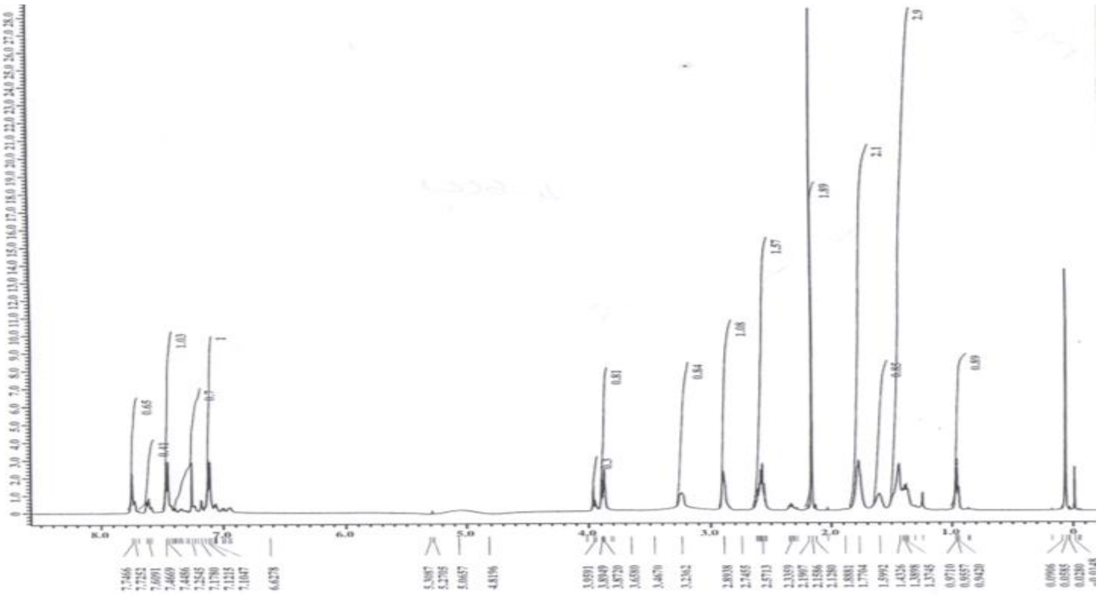


Figure 1: FT-IR spectra of polymer $P_1$

### 3.1.2 $^1H$ NMR Spectroscopy:

The structure of polymers was also analysed by $^1H$ NMR spectroscopy. All the polymers show a doublet around 6.9 δ corresponds to olefinic protons and aromatic protons appearing as a multiplet at 7.1 – 8.2 δ. Polymers show a singlet peak at round

3.6 δ due to –$OCH_3$ protons. The representative $^1H$ NMR spectrum of polymer $P_1$is shown in figure 2.

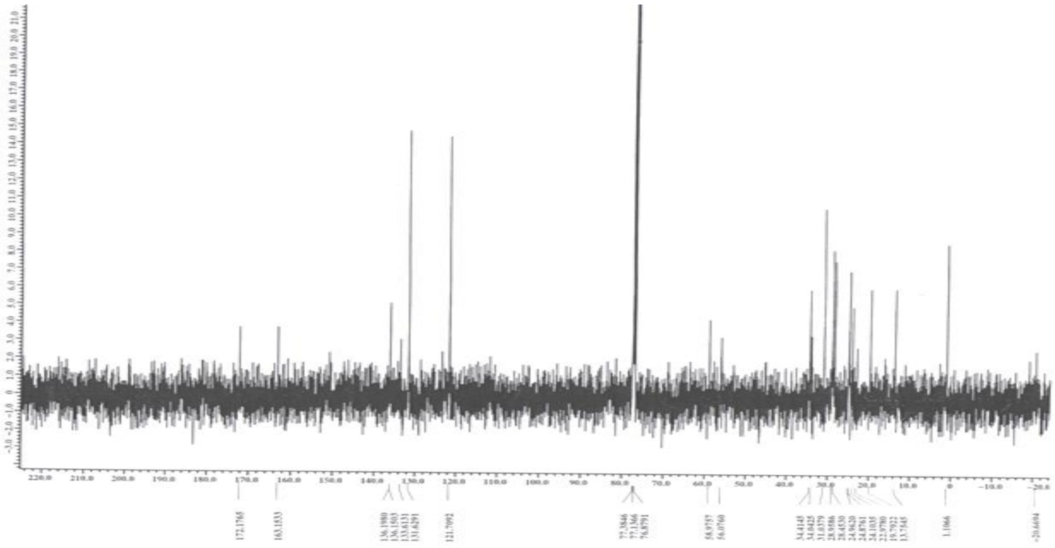


**Chemical shift (δ)**

Figure 2: $^1H$ NMR spectra of polymer $P_1$

### 3.1.3 $^{13}C$ NMR Spectroscopy

A typical proton decoupled $^{13}C$ NMR spectrum of polymer $P_1$ is shown in figure 3. The polymer shows resonance signal at 189.5 δ due to ketone carbonyl carbon. The signal at 172 δ corresponds to ester carbonyl carbon. The aromatic carbons attached to the ester oxygen exhibit resonance signals at 150 δ. The other aromatic carbons resonate around 136 δ. The methylenic, -$CH_2$-, carbon signals are observed at 24.2 and 34.0 δ. The methoxy carbon shows resonance signal[17, 18] at 56.0 δ. The above spectral results confirm the formation of polymers.



**Chemical shift (δ)**

Figure 3: $^{13}C$ NMR spectrum of polymer $P_1$

### 3.2 Thermal Studies:

The thermal property of the polymers was studied by differential scanning calorimetry. The DSC analysis revealed that the melting temperatures ($T_m$) of the polymers were decreased with an increase in the flexible methylene chain length in the polymeric structure.

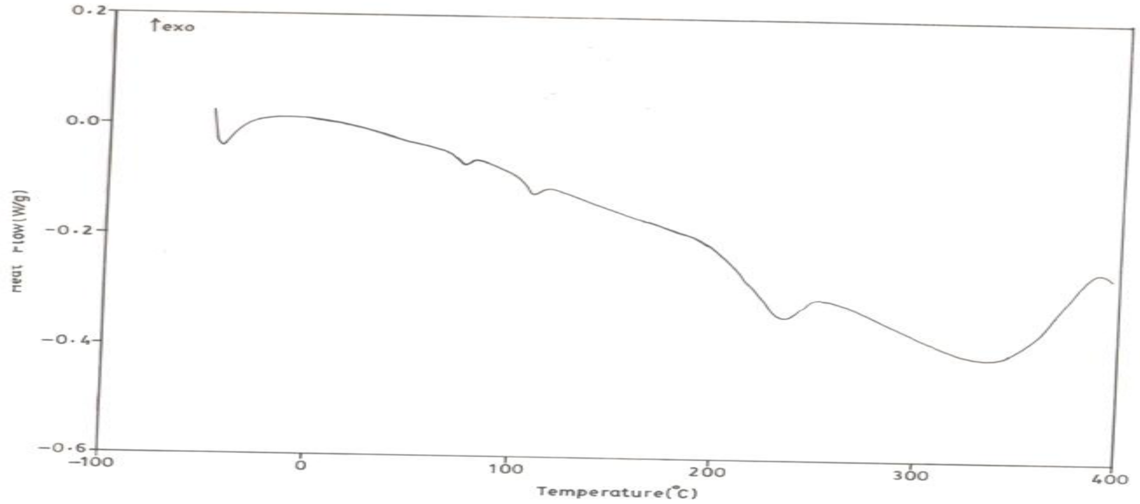


Figure 4: DSC trace of polymer $P_1$

These polymers also exhibit multiple meltings due to enhanced flexibility offered by the methoxy group and due to melting of crystalline units inside the hard macrodomains[19].

### 3.3 Reason for used phase transfer catalyst of TBABr

The polycondensation in an organic solvent without phase transfer catalyst is not suitable for the synthesis of high molecular-weight polyesters because the resulting oligomer precipitates[20] at the initial stage of the reaction. Both the yield and molecular weight of random copolyesters are increased when PTC is used as catalyst, because the complex of phase transfer catalyst with phenolate is difficult to diffuse from the water phase to the organic phase. When a quaternary ammonium salt is added, it acts as a phase transfer catalyst and accelerates the transportation of reactants from the aqueous phase to the organic phase[21].

The yield increases with the concentration of the catalyst but only up to a certain level above which the yield remained almost constant. The experimental results in Table 4.13.2.show that the molecular weight of polyesters increases in the order $Cl^-<Br^-<I^-$. The salvation of anion is an important factor for liquid phase reactions. In a protic solvent like $CH_2Cl_2$, would have stronger salvationmay be expected[22].

| Polyester Code | PTC | Reaction media | Yield (%) | $M_w$ |
|---|---|---|---|---|
| $P_1$ | TBABr | $H_2O/CH_2Cl_2$ | 78.8 | 22800 |
| $P_2$ | TBACl | $H_2O/ CH_2Cl_2$ | 75.6 | 20800 |
| $P_3$ | TBAI | $H_2O/ CH_2Cl_2$ | 79.2 | 30600 |
| $P_4$ | 15-C-5 | $H_2O/ CH_2Cl_2$ | 15.6 | 8500 |

TBACl = Tetrabutyl ammonium chloride
TBABr = Tetrabutyl ammonium bromide
TBAI = Tetrabutyl ammonium iodide
15-C-5 = 15-crown-5

### 3.4 Role of the Solvent:

When cyclohexane, carbon tetrachloride or benzene with low polarity is used as the organic phase, the molecular weight of polymer is not high. On the other hand, high molecular weight is attained when a more polar organic solvent such as dichloromethane, nitrobenzene and chloroform is used[23].

## 4. Conclusions:

Aliphatic and aromatic polyester was synthesised by interfacial polycondensation using phase transfer catalyst. The structure of monomer and polymers were confirmed by spectroscopic techniques. The thermal stability of the polymers was found to vary with types of diol.

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