

A study on photo active bischalcone based liquid crystalline polyesters

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Abstract:-- A new series of polymer derived from bischalconediol with some diacids was synthesized by polycondensation reaction using 3, 3'- (1, 4-phenylene)bis(4-hydroxyphenyl)prop-2-en-1-one) with terephthalic acid, succinic acid and glutaric acid. The diacids are converted to their respective diacid chlorides, which are then used to esterify the phenolic moiety of the bischalcone diols. The polyesters obtained were characterized by using IR and the polymer-solvent dipolar interaction was studied by dissolving in various solvents. The UV spectral studies showed the existence of conjugated system due to the transition in the $\pi \rightarrow \pi^*$ region. Further the decrease in the absorbance upon irradiation shows that the double bonds present in the molecule undergoes photocycloaddition reaction. The thermal behaviour of the polymer were studied using DSC thermograms. The anti bacterial activity was also studied and the polymers have shown good antibacterial activity.

Keyword:-- Liquid crystalline polymers, polyester synthesis, polycondensation.

1. INTRODUCTION

Chalcones(trans- 1,3-diaryl-2-propen-1-ones), belong to flavanoid family. They are the precursors of open chain flavonoids and isoflavonoids, which are present in edible plants. Chalcones are also key precursors in the synthesis of many biologically important heterocycles such as benzothiazepine, pyrazoline, 1,4-diketones and flavones. They show antibacterial, antifungal, antitumour and anti-inflammatory property[1]. Chalcone diols have been exhaustively used as monomers in the synthesis of polymers. The polymers have shown encouraging antimicrobial activity, cross-linking ability, non-linear optical property and liquid crystalline [2,3] property.

Thus the synthesis of chalcones has generated vast interest to organic as well as to medicinal chemists. The traditional methods for the synthesis of chalcones involves the use of strong bases such as NaOH, KOH, Ba(OH)₂, hydrotalcites, LiHMDS, calcined NaNO₃/natural phosphate. There are also some reports of acid- catalysed aldol condensations, e.g. AlCl₃, BF₃, dry HCl, ZrH₂/NiCl₂ and RuCl₃(for cyclic and acyclic ketones). In this present work, it is proposed to synthesize three copolyester [4] by the reaction of bischalcone diol with each of the three varying acids. The following are the three varying diacids viz. terephthalic acid, succinic acid and glutaric acid.

2. EXPERIMENTAL STUDY

The monomers, solvents and other reagents used for the synthesis and characterization of the polymers and the

procedure adapted for their synthesis are described in this chapter.

2.1. Monomer synthesis

2.1.1. Preparation of (Bischalcone diol)

Dry hydrochloric acid gas was passed through a solution containing 4-hydroxyacetophenone (Loba) (2.72 g) and terephthalaldehyde (Ranbaxy) (4.4 g) in dry methanol. The solution turned dark pink and yellow precipitate was obtained after the addition of water. It was purified by recrystallization from methanol.

2.1.2. Preparation of diacid chlorides

About 5 g of Terephthalic acid(Aldrich), Succinic acid(Merck) and Glutaric acid(Aldrich) was taken in a 50 ml RB flask. About 8 ml of Thionylchloride (SpectochemAR) was added to each of them. It was allowed to stand for 24 hours. The excess thionyl chloride was removed by suction at the suction pump for about 5 hours.

2.2. Synthesis of polymers:

2.2.1. Polymer BCTA

About 2g of Terephthaloylchloride was dissolved in DMF. Bischalconediol(1g) was also dissolved in a minimum amount of DMF[5]. The two solutions were mixed and about 1ml of triethyl amine(SpectochemAR) was added and stirred well. The solution is left undisturbed for about 1 day. Then it is filtered and dried.

2.2.2. Polymer BCSA

About 2g of Succinylchloride was dissolved in DMF. Bischalconediol(1 g) was also dissolved in a minimum amount of DMF. The two solutions were mixed and about 1ml of triethyl amine(SpectochemAR) was added and stirred

well. The solution is left undisturbed for about 1 day. Then it is filtered and dried.

2.2.3. Polymer BCGA

About 1g of glutarylchloride was dissolved in DMF. Then, about 1g of bischalconediol was also dissolved in a minimum amount of DMF. The two solutions were mixed and about 1ml of triethyl amine(SpectochemAR) was added and stirred well[5]. The solution is left undisturbed for about 1 day. Then, it is filtered and dried.

2.3. Methods of analysis

The UV-visible spectra were recorded on a JASCO variant 530 spectrophotometer, at V.O.C. College, Thoothukudi. The infrared spectra of the polymers have been recorded in a Nicolet iS5 spectrophotometer, in solid phase, as ATR in V.O.C. College, Thoothukudi.

The DSC thermograms were recorded at S.F.R College, Sivakasi. The solubility of the polymers was tested with various organic and inorganic solvents[6,7].

2.4. Photocrosslinking studies

A small amount of the substance is dissolved in DMF. It is diluted to get a meaningful absorption in the UV spectrophotometer. The solution in the quartz cuvette was exposed to tungsten light in a closed white box in regular intervals of time. After every exposure the absorbance was measured at the UV spectrophotometer[1, 2, 8]. The decrease in absorbance was determined by overlaying the recorded spectra.

2.5. Antibacterial Assay

Stock cultures of bacteria such as Sterptococcus fecalis, Sterptococcu spyogens, Salmonella paratyphi and Pseudomonas aeruginosa were obtained from Research Laboratory, Department of botany, V.O.C. College, Thoothukudi.

2.5.4. Antimicrobial activity

Antimicrobial activity was demonstrated by modification of the method described by Barry and Thornsberry, (1985). 0.1 ml of the diluted microbial culture was spread on sterile nutrient agar plate. The presoaked and dried discs of 6mm diameter of What man No.1 filter paper were then placed on the seeded plates and gently pressed down to ensure contact. At the same time standard antibiotic of Tetracycline was used as reference or positive control. Respective solvents without plant extracts served as negative control. The plates were incubated at 37oC for 24 hours. After the incubation period, the diameter of the inhibition zone around the plant extract saturated discs were measured and also compared with the diameter of inhibition zone of

commercial standard antibiotic discs [9-13].The inhibition zone around the discs were measured and recorded as the difference in diameter between the disc (6mm) and growth free zone.

3. RESULTS AND DISCUSSION

The aim of the present work is to synthesize new thermotropic liquid crystalline polymers by solution polycondensation reaction[14-15] with bischalcone and three diacids. The chalcone is planned to be synthesized by method reported by Kannappan et al [16].

Table 1:
The monomers and their corresponding polymer codes[17,18]

MONOMERS	POLYMER CODE
Bischalconediol, Terephthalic acid	BCTA
Bischalconediol, Succinic acid	BCSA
Bischalconediol, Glutaric acid	BCGA

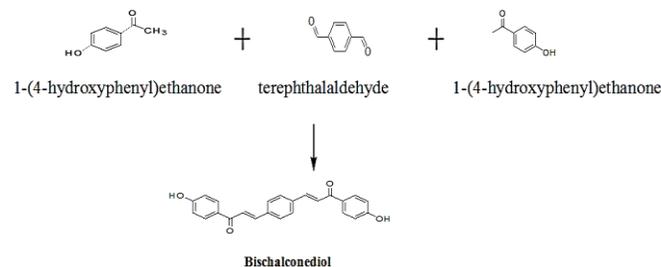
The scheme of synthesis is discussed below:

To a methanolic solution of 1-(4-hydroxyphenyl) ethanone and terephthalaldehyde dry HCl gas is made to pass and the resultant bischalcone [1] was used for the synthesis of the polyesters.

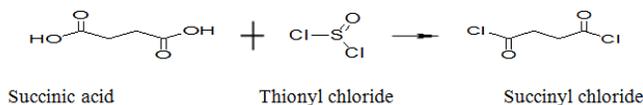
The diacids are to be converted to their respective diacid chlorides, which can be used to esterify with the phenolic moiety of the bischalconediols.

The intended polymers are to be prepared by the following schemes

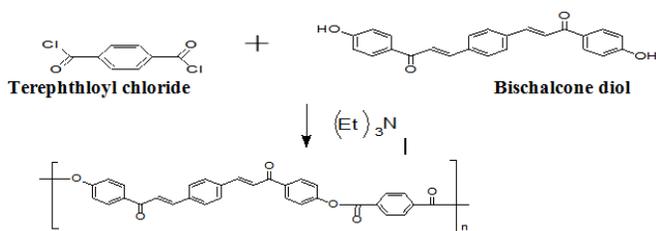
Scheme 1. Preparation of bischalconediol (common monomer)



Scheme 2. Preparation of diacid chlorides



Step 3. Synthesis of co-polyesters



BCTC

Molecular weight, rigidity of polymer backbone and polymer-solvent dipolar interactions are the three factors which influence solubility of polymers. The solubility of the compounds was determined qualitatively in a variety of solvents and the observations are presented in the table below.

Table 2
Solubility characteristics of the bischalcone based polymers

S.No.	Solvent	BCTA	BCSA	BCGA	S.No.	Solvent	BCTA	BCSA	BCGA
1	DMF	++	++	++	6	Chloroform	++	++	++
2	DMSO	++	++	++	7	Methanol	+.	+.	+.
3	Benzene	++	++	++	8	Ethanol	+.	+.	..
4	Toluene	++	++	++	9	Water	+.
5	Ether	++	++	++					

++ soluble +. sparingly soluble, .. insoluble

3.1. Polymer characterization

The polymers were characterized using IR spectroscopy[19, 20]. The carbonyl stretching in the compounds is indicated by absorption at $\nu=1643-1688 \text{ cm}^{-1}$. It may be noted that the absorption at this region indicates that chalcone moiety is incorporated.

There is an absorption in the range $\nu = 1723 - 1752 \text{ cm}^{-1}$ in the IR spectra of each of the polymer which is due to the carbonyl stretching of the ester group [21]. This confirmed the formation of ester linkage as shown in Fig.1 and Fig.2. In other words the formation of the polymers. The strength of this signal is rather weak, against the authors' expectation. This may be due to relative intensity with that of carbonyl and aromatic stretching signals. The absorption in the range of $\nu = 1535 \text{ cm}^{-1}$ is due to olefinic and aromatic C=C stretching.

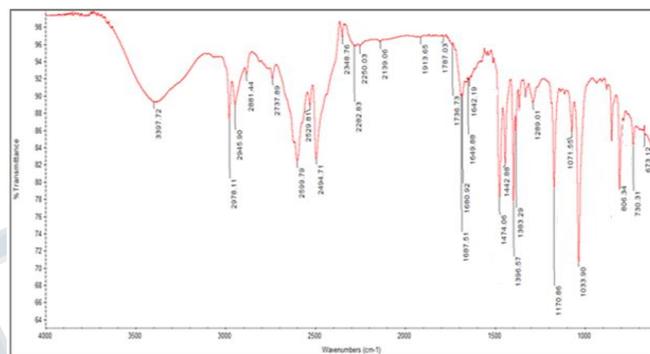


Fig. 1. IR spectra of BCTA

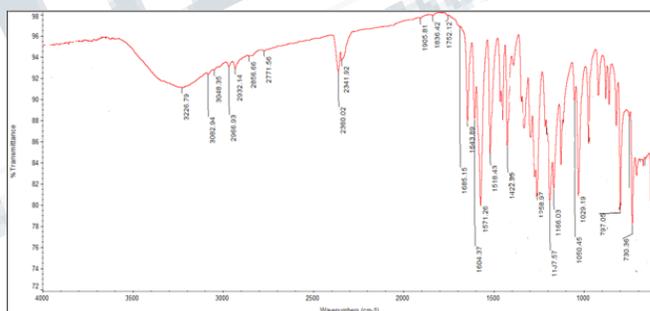


Fig. 2. IR spectra of BCGA

The UV spectra of the compounds were recorded in DMF. The polymers show the following absorption bands. These absorptions are attributed to $\pi \rightarrow \pi^*$ electronic transition in the conjugated system of the polymers. The absorption values are 346 nm for BCTA, 360nm for BCSA and 340nm for BCGA which can be seen in Fig.3 and Fig.4.

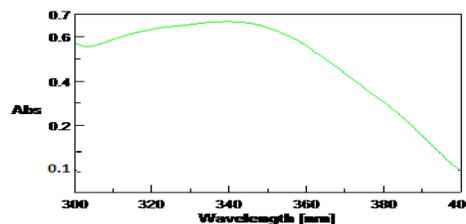


Fig.3. UV spectra of BCTA

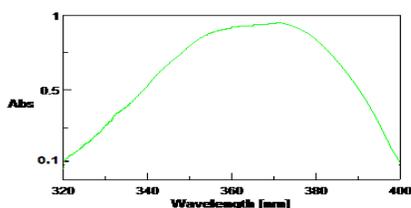


Fig 4. UV spectra of BCSA

3.2. Photo crosslinking studies

The double bonds present in the molecules undergo photocycloaddition reaction[3, 22]. This is established by decrease in the absorbance value at the respective absorptions due to the irradiation of light from an incandescent light. For this the compounds were dissolved in DMF.

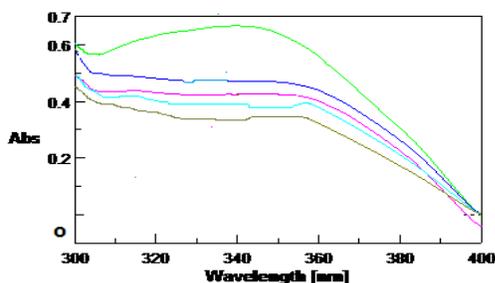


Fig.5. Photocrosslinking in BCTA

The absorption band in the range 340-360 nm corresponds to the $\pi \rightarrow \pi^*$ transition of the exocyclic double bond. During the successive irradiations, a decrease in the intensity of the absorbance was observed as shown in Fig.5 and Fig.6. This may be due to the photo-crosslinking [23-25] of the polymer chains, which involves the $2\pi + 2\pi$ cycloaddition reaction of the double bond leading to formation of cyclobutane rings.

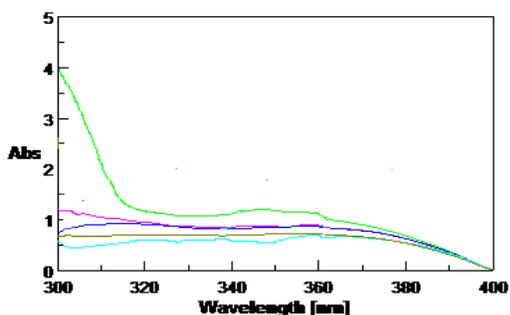


Fig.6. Photocrosslinking in BCSA

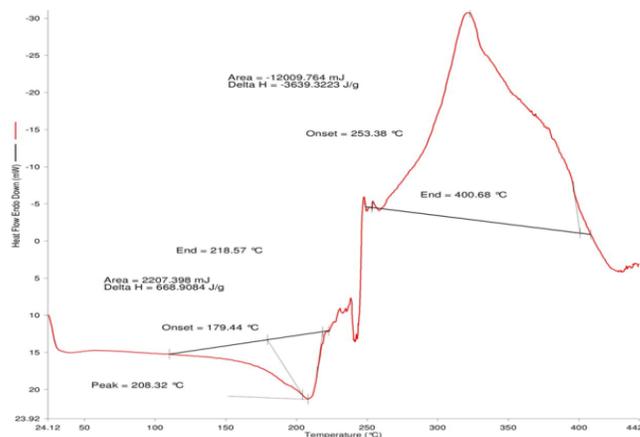


Fig.7. DSC thermo gram of BCTA ($T_g - 450^{\circ}C$, $T_m - 2100^{\circ}C$, $T_c - 1100^{\circ}C$)

3.3. Thermal behaviour studies

Thermal studies have an important role in studying the thermotropic nature of polymers. The thermal behavior of the polymers plays an important role in determining the specific use of the polymers. DSC studies were widely used to study about thermodynamic properties of the polymers like enthalpy and of the polymer[26-29]. The glass transition temperature of the polymers can be studied using DSC. The T_g values vary with the change in microstructure of the polyesters.

The T_g values lie above the room temperature, for some very close to the room temperature, which is an encouraging result. The melting temperature ranges from 130 to 240, which are again not so high with regards to processing temperature in industries. Thermotropic liquid crystals show liquid crystalline behaviour above the melting point of their crystallites[30]. All the polymers exhibited liquid crystalline behaviour which can be seen in Fig.7 and Fig.8.

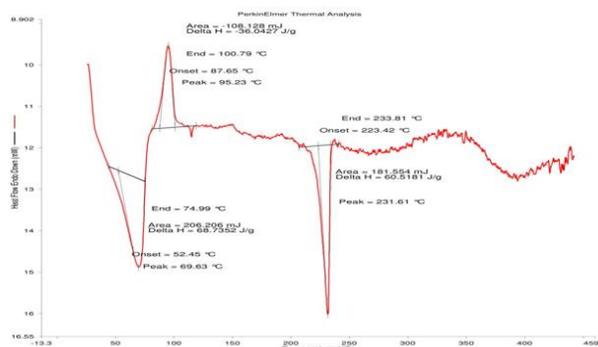


Fig.7. DSC thermo gram of BCSA ($T_g - 75^{\circ}C$, $T_m - 235^{\circ}C$, $T_c - 190^{\circ}C$)

3.4. Antimicrobial studies

The bacterial efficiency of the compounds was screened for *Pseudomonas aeruginosa*, *Streptococcus fecalis*, *Streptococcus pyogenes* and *Salmonella paratyphi*, by disc diffusion methods. The zone of inhibition for the polymers were shown below.

Table 3

Polymers and their zone of inhibition(mm) on different microbes

	BCTA	BCSA	BCGA
Streptococcus fecalis	15	10	17
Streptococcus pyogens	15	13	18
Pseudomonas aeruginosa	21	10	10
Salmonella paratyphi	10	11	11

CONCLUSION

A new series of bischalcone based polymers were synthesized, characterized and studied. The polymerization reaction between bischalcone and the three diacids have been confirmed by IR studies. The UV and photo cross-linking studies proved the existence of conjugated double bond and its ability to undergo photo cycloaddition reaction. The DSC thermograms showed that the polymer has good thermal behaviour which can be used in industry. The antimicrobial activity of the polymers were also studied.

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