

Synthesis and Characterization of Certain Thermotropic Liquid Crystalline Copolyesters Containing α , β - Unsaturated Ketone in the Main Chain

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Abstract

A series of six copolyesters were synthesized by phase transfer catalyzed condensation of adipoyl chloride with 1, 3-bis(4-hydroxyphenyl)propanone as the common diol (diol-1) and arylidene diols as the varying diols (diol-2). The common diol and the six varying diols were prepared by acid catalyzed Claisen-Schmidt reaction. The synthesized copolyesters were characterized by solubility data and viscosity values. The microstructure of the repeating unit present in the copolyester chain was confirmed by FTIR, ¹H NMR and ¹³C NMR. Thermal transition temperatures were determined from the DSC thermogram. Optical polarizing microscopy was used to establish the liquid crystalline property. Since these copolyesters contain α , β -unsaturated ketones in the main chain they may emerge as UV shielding materials.

Keywords: Copolyesters, Claisen-Schmidt Reaction, Condensation, Viscosity

Introduction

An extensive literature survey reveals that arylidene-ketone-based polymers or chalcone-based polymeric materials facilitated the existence of liquid crystalline property. Borden [1] has synthesized a series of photocrosslinkable polymers containing arylidene-keto moiety in the main chain. They are used in photo-resists

and photolithographic applications. Kishore and coworkers [2, 3] have found that polymers with arylidene-keto moiety possessed photocrosslinkable property which could be exploited in NLO applications. Kannan and coworkers [4-6] have reported the synthesis and characterization of photocrosslinkable phosphoramidate esters and aryl phosphate esters. The linear unsaturated polyphosphate esters based on divanillylidene cycloalkanone possessing photocrosslinkable properties were studied by Sakthivel and coworkers [7, 8]. Arumugasamy [9] has synthesized a number of random copolyesters containing 4, 4'-dihydroxybis(arylidene)cyclopentanones using aliphatic diacid chlorides and found that they exhibited thermotropic liquid crystalline (TLC) behaviour by optical polarizing microscopic studies. Kannappan et al. [10] investigated the rate of photocrosslinking of the random copolyesters with arylidene-keto moiety by UV spectral studies.

Unrush et al. [11] synthesized photocrosslinkable polymers containing chalcone moieties and investigated their crosslinking behaviour using UV spectroscopy. Kato et al. [12] demonstrated the photosensitive properties of certain polymers containing chalcones. Chudger et al. [13] prepared a series of polyesters comprising dihydroxy bischalcones. Kaniappan et al. [14] has reported the synthesis of some phosphorus-based polymers and photosensitive polyesters containing monochalcone moiety in the main chain and studied the kinetics of their crosslinkability by UV spectroscopy. Choi et al. [15-17] synthesized bifunctional epoxy compound and dimethyl acrylate compound containing a chalcone moiety in the main chain. Sadafule and coworkers [18] synthesized vinyl polyesters. Ya-Dong et al. [19] synthesized and characterized the hole-transport polymers with cinnamate and chalcone groups as photocrosslinking moieties. Sung et al. [20] incorporated chalcone moiety in the copolymer backbone and carried out photocrosslinkable studies. Nosova et al [21] prepared a large number of light-sensitive polymers using chalcone diols.

However, there are no reports on the synthesis of random copolyesters containing arylidene keto moiety and chalcone moiety in the main chain. We report herein the synthesis of certain random copolyesters containing arylidene-keto moiety and chalcone moiety in the main chain.

Experimental

Synthesis of 1, 3-bis(4-hydroxyphenyl)propenone (BHPP)

The chalcone diol BHPP was synthesized by the method reported by Chitra and coworkers [22].

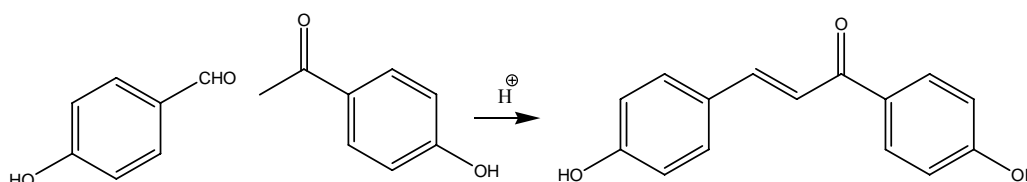


Figure 1: Reaction scheme for the synthesis of 1, 3-bis(4-hydroxyphenyl)propenone (BHPP)

Dry HCl gas was passed through a well-cooled and stirred solution of 4-hydroxybenzaldehyde (60 mmol) and 4-hydroxyacetophenone (60 mmol) in 20 mL of dry methanol. Yellow crystals of BHPP separated. It was washed with double distilled water and re-crystallized from hot methanol. Yield: 90% m.p.:197.2°C; IR (KBr) 3301 (b, O-H), 1648(s, C=O) cm^{-1} ; $^1\text{H NMR}$ (DMSO- d_6) δ 9.91 (s, 2H, -OH), δ 7.42–8.46 (m, 8H, aromatic), δ 6.71–6.95 (dd, 2H, -CH=CH-) and; MS (EI) m/z 240 $[\text{M}]^+$.

Synthesis of diol - 2 (Arylidene Diols)

The six arylidene diols (BHAC, BVAC, BHCP, BVCP, BHCH and BVCH) were synthesized by the method reported by Kannappan and coworkers [10].

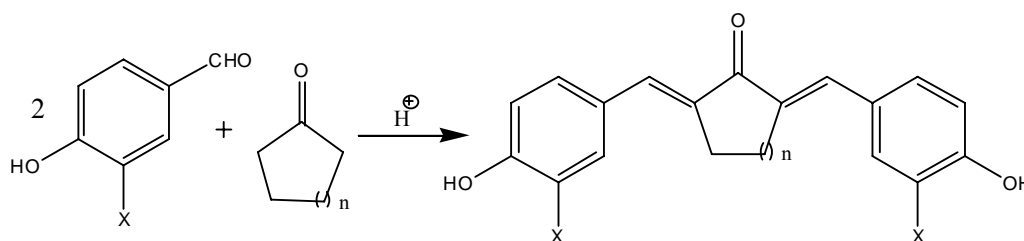


Figure 2: Reaction scheme for the synthesis of arylidene diols

Arylidene diol	Benzaldehyde	Ketone
BHAC	X = H	Acetone
BVAC	X = OCH ₃	Acetone
BHCP	X = H	n = 1
BVCP	X = OCH ₃	n = 1
BHCH	X = H	n = 2
BVCH	X = OCH ₃	n = 2

Preparation of 1, 5-bis(4-hydroxyphenyl)penta-1, 4-dien-3-one (BHAC).

Dry HCl gas was passed through a well-cooled solution of 4-hydroxybenzaldehyde (60 mmol) and acetone (30 mmol) in 50 mL of dry methanol with stirring. Green crystals of HBAC were separated. It was filtered, washed with distilled water and re-crystallized from hot methanol. Yield: 94% m.p.241°C; IR (KBr) 3448 (b, O-H), 1658(s, C=O) cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl₃) δ 6.62–6.98 (dd, 4H, -CH=CH-), δ 7.20–8.57 (m, 8H, aromatic) and 9.97 (s, 2H); MS (EI) m/z 266 $[\text{M}]^+$.

Preparation of 1, 5-bis(4-hydroxy-3-methoxyphenyl)penta-1, 4-dien-3-one (BVAC)

Dry HCl gas was passed through a well-cooled solution of vanillin (60 mmol) and acetone (30 mmol) in 50 mL of dry methanol with stirring. Yellow crystals of BVAC were separated. It was filtered, washed with distilled water and re-crystallized from

hot methanol. Yield: 94% m.p. 161°C; IR (KBr) 3446(b, O-H) 1658(s, C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.45 (s, 6H), δ 6.60–7.05 (dd, 4H, -CH=CH-), δ 7.33–8.62 (m, 6H, aromatic) and 9.97 (s, 2H); MS (EI) m/z 326 [M]⁺.

Preparation of 2, 5-bis(4-hydroxybenzylidene)cyclopentanone (BHCP)

Sulphuric acid (1 mL) was added in drops to a well-cooled solution of 4-hydroxybenzaldehyde (60 mmol) and cyclopentanone (30 mmol) in 50 mL of dry methanol with occasional shaking. Green crystals of BHCP separated. It was washed with aqueous methanol and re-crystallized from hot methanol. Yield: 90% m.p. >300°C; IR (KBr) 3438 (b, O-H), 1648(s, C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.92 (s, 4H), 6.79–7.49 (m, 10H) and 9.97 (s, 2H); MS (EI) m/z 292 [M]⁺.

Preparation of 2, 5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (BVCP)

Sulphuric acid (1 mL) was added in drops to a well-cooled solution of vanillin (60 mmol) and cyclopentanone (30 mmol) in 50 mL of dry methanol with occasional shaking. Yellow crystals of BVCP separated. It was washed with aqueous methanol and re-crystallized from hot methanol. Yield: 88% m.p. 212°C; IR (KBr) 3448(b, O-H) 1654(s, C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.92 (s, 4H), 3.42 (s, 6H), 6.72–7.50 (m, 10H) and 9.94 (s, 2H); MS (EI) m/z 352 [M]⁺.

Preparation of 2, 6-bis(4-hydroxybenzylidene)cyclohexanone (BHCP)

Sulphuric acid (1 mL) was added in drops to a well-cooled solution of 4-hydroxybenzaldehyde (60 mmol) and cyclohexanone (30 mmol) in 50 mL of dry methanol with occasional shaking. Green crystals of BHCH separated. It was washed with aqueous methanol and re-crystallized from hot methanol. Yield: 90% m.p. 278°C; IR (KBr) 3438 (b, O-H), 1648(s, C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.92 (s, 4H), 6.79–7.49 (m, 10H) and 9.97 (s, 2H); MS (EI) m/z 306 [M]⁺.

Preparation of 2, 6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone (BVCH)

Sulphuric acid (1 mL) was added in drops to a well-cooled solution of vanillin (60 mmol) and cyclohexanone (30 mmol) in 50 mL of dry methanol with occasional shaking. Yellow crystals of BVCH separated. It was washed with aqueous methanol and re-crystallized from hot methanol. Yield: 86% m.p. 182°C; IR (KBr) 3442(b, O-H) 1652(s, C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.92 (s, 4H), 3.45 (s, 6H), 6.79–7.49 (m, 10H) and 9.97 (s, 2H); MS (EI) m/z 366 [M]⁺.

Synthesis of Copolyesters

The six copolyesters were synthesized by the method reported by Samuel and coworkers [24]. The procedure for the synthesis of typical aliphatic diacid-based copolyester is given here. The common diol also called as diol-1 namely BHPP, (2.5 mmol) and the varying diol also called as the diol-2 BVCH, (2.5 mmol) were dissolved in double distilled water (25 mL) containing dissolved sodium hydroxide (10 mmol) taken in a three necked 100 mL round bottomed flask. The mixture was stirred continuously at room temperature for 30 minutes in nitrogen atmosphere. A solution of 2 mL of 2% tetra-n-butylammonium bromide was added and stirred. About 25 mL solution containing the adipoyl chloride (5 mmol) in dichloromethane

was added using a pressure equalizer with constant stirring. The mixture was maintained at room temperature with continuous stirring for 3 hours. The reaction mixture was poured into 300 mL of methanol when the copolyester was precipitated. It was filtered, washed with methanol and then dried at vacuum pump.

The monomer diols and diacid chloride used and the copolyester code of the six copolyesters are represented in table 1.

Table 1: The codes used for variable diols and copolyesters

Common diol (Diol – 1) - 1, 3-bis(4-hydroxyphenyl)propanone Diacid chloride - Adipoyl chloride	
Variable diol (Diol – 2)	Copolyester Code
BHAC	PHAA
BVAC	PHBA
BHCP	PHCA
BVCP	PHDA
BHCH	PHEA
BVCH	PHFA

Characterization of Copolyesters

The solubility of these copolyesters was tested in various solvents qualitatively. Inherent viscosities were determined for these copolyesters at 30°C in DMAc of concentration 0.1 gL⁻¹ using Ubbelohde viscometer. IR spectra of the copolyesters were recorded using Shimadzu 8400 instrument. The ¹H and ¹³C NMR spectra of the copolyesters were recorded with Bruker instrument in DMSO-d₆ solvent. DSC thermograms were recorded with Dupont 2000 model instrument, at a heating rate of 10°C/min under nitrogen atmosphere. Optical polarizing micrographs were obtained from Euromex polarizing microscope equipped with a Linkem HFS 91 heating stage and a TP-93 temperature programmer.

Results and Discussion

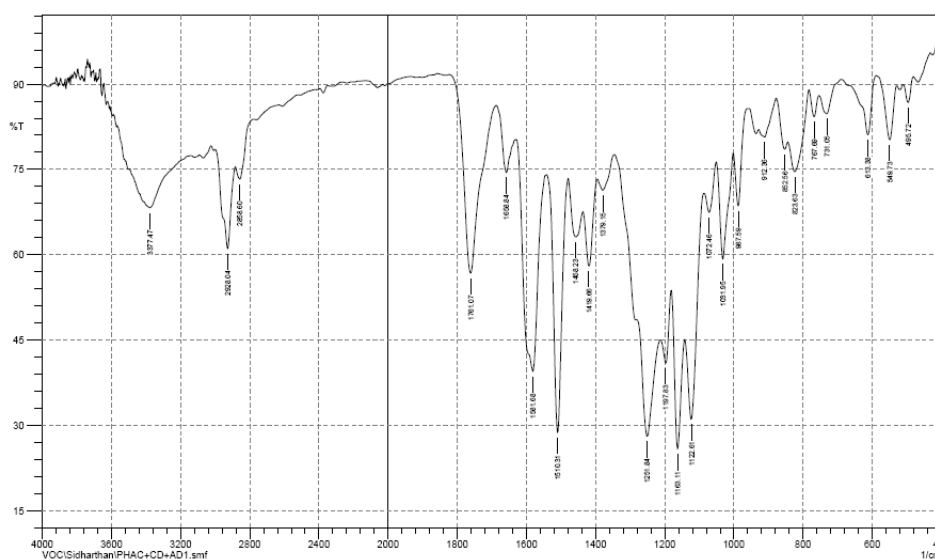
The six copolyesters synthesized in the present work were characterized by viscosity measurements and spectral data. Thermal transition temperatures like T_g, T_m and T_{cl} were determined from DSC thermogram. The type of mesophase generated was understood from optical polarizing microscopy at elevated temperature.

The solubility of these copolyesters was tested in various solvents qualitatively and was found to be soluble in polar solvents such as dimethylsulphoxide and dimethylacetamide but insoluble in non polar solvents like hexane and benzene. The inherent viscosity value indicates that the outcome of the copolyester synthesis is successful.

Table 2: Percentage yield and inherent viscosities (η_{inh}) of the copolyesters

Copolyester Code	Percentage Yield %	Inherent Viscosities η_{inh} (dL/g)
PHAA	64	0.40
PHBA	67	0.44
PHCA	75	0.45
PHDA	78	0.49
PHEA	78	0.48
PHFA	78	0.53

The ester functional group present in the copolyester chain was identified by FTIR spectra. The FTIR spectra of all the copolyesters showed characteristic absorption in the range of $\bar{\nu} = 1735\text{-}1761\text{ cm}^{-1}$ due to ester C=O stretching frequency which clearly indicates the polymerization. A typical FTIR spectrum of PHFA copolyester is given in figure 3.

**Figure 3:** FTIR spectrum of PHFA copolyester prepared from BVCH variable diol and 1, 3-bis(4-hydroxyphenyl)propanone common diol

The structural units present in the polymer chain were identified by ^1H and ^{13}C NMR spectra. The aromatic protons are observed in the range of 7.0 and 8.3 ppm. The methoxy protons in the vanillin moiety are indicated by a signal at 3.4 ppm. A signal at 2.1 ppm is attributed to the methylene protons of the cyclopentanone ring. The central $-\text{CH}_2-$ groups in adipoyl moiety appeared at 1.7 ppm.

The signals in the range of δ 172-185 ppm, δ 165-170 ppm and δ 150-162 ppm

in the ^{13}C NMR spectra of the copolyesters are due to the carbonyl carbon of the cyclopentanone moiety, carbonyl carbon of chalcone moiety and ester group which indicates the formation of copolyester.

Thermal Characterization

DSC thermograms for all the six copolyesters are shown in figure 2. These thermograms were used to determine the thermal transition temperatures like the glass transition temperature (T_g), mesophase formation temperature (T_m) and clearing temperature (T_{cl}).

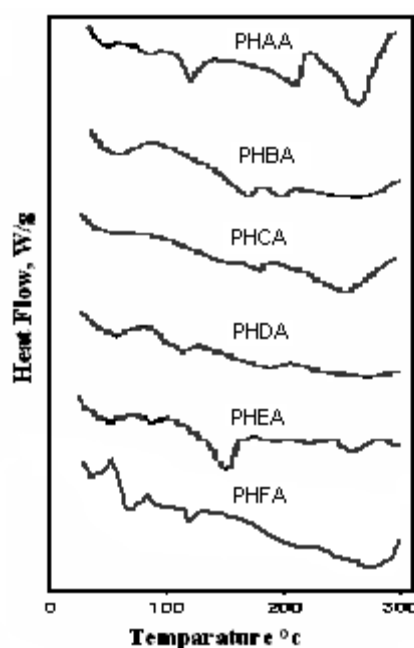


Figure 4: DSC thermograms for all the six copolyesters

The thermal transition values of each copolyester obtained from the figure 2 are represented in table 3.

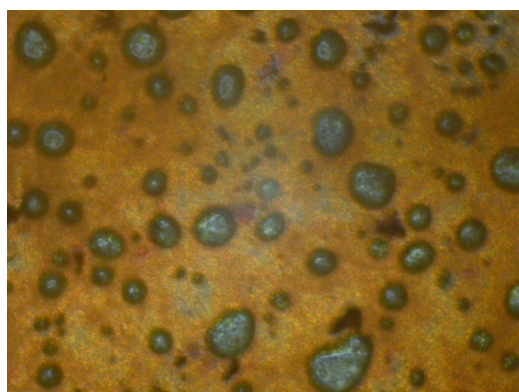
Table 3: Thermal data of the six copolyesters with their respective codes

Copolyester Code	T_g (°C)	T_m (°C)	T_{cl} (°C)
PHAA	36.0	66.5	120.0
PHBA	47.5	106.0	164.0
PHCA	48.0	88.5	183.5
PHDA	49.5	99.0	178.5
PHEA	48.5	80.5	151.0
PHFA	53.5	96.5	188.0

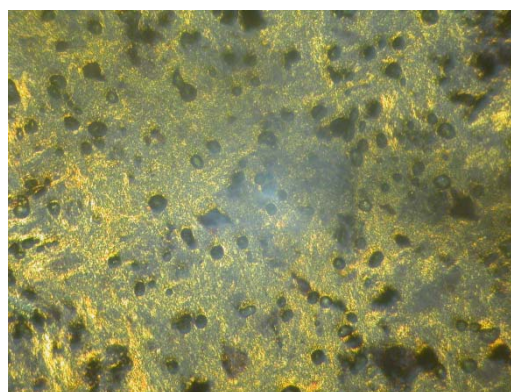
The thermograms showed that the thermal transition temperatures are found to be less than 200°C which may be due to the presence of flexible methylene groups. An interesting observation in the present work is that the copolyesters derived from vanillin-based arylidene diols have higher T_g than the copolyesters obtained from 4-hydroxybenzaldehyde-based arylidene diols which may be due to the interlocking effect of the methoxy substituent present in the aromatic ring. Similar observation was made by Samuel and coworkers in a series of copolyesters derived from arylidene diols having methoxy substituents [23]. Even in the case of T_m and T_{cl} values the copolyesters synthesized from 4-hydroxybenzaldehyde-based arylidene diols have lower values than the copolyesters obtained from vanillin-based arylidene diols.

Optical Polarizing Microscopy Studies

The mesophase formation was identified by using optical polarizing microscopy and the optical polarizing micrographs are shown in figures 5, 6 and 7. The micrographs show that the copolyester displayed nematic phase. This may be due to the presence of bisbenzylidene and chalcone moieties incorporated in the copolyester backbone. Similar observation was made by Kannan and coworkers [24] in a series of copolyesters which displayed nematic liquid crystalline phases and the development of grainy to Schlieren textures depends on the length of flexible spacer in the polymer backbone which was in accordance with DSC analysis.



PHCA photo taken at 123°C



PHEA photo taken at 183°C



PHDA photo taken at 105°C

Conclusion

A series of six copolyesters were synthesized using a diacid chloride, diol-1 and diol-2. The dicarboxylic acid chloride used is adipoyl chloride, the diol-1 used is BHPP. The diol-2 used are BHAC, BVAC, BHCP, BVCP, BHCH and BVCH. The copolyesters were characterized by viscosity and spectral data. DSC thermograms were employed to identify the thermal transition temperatures. The OPM studies indicate the type of mesophase formed.

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