ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF CERTAIN PHOTOCROSSLINKABLE RANDOM COPOLYESTERS WITH BISCHALCONE MOIETY

T.S.PERUNDEVI[1], D. REUBEN JONATHAN[2] AND S. KOTHAI*[1]

1. PG & Research Department of Chemistry, Ethiraj College for Women, Chennai – 600 008, India.
2. Department of Chemistry, Madras Christian College, Chennai – 600 059, India.

Manuscript Info

Manuscript History:

Received: 12 January 2015
Final Accepted: 22 February 2015
Published Online: March 2015

Key words:

Bischalcone, Copolyester, Photocrosslinking, Liquid Crystalline

Corresponding Author

T.S.PERUNDEVI

Abstract

Six novel random copolyesters with bischalcone moiety in main chain were synthesized using direct polycondensation method. A common diol namely 1,5-dihydroxyanthraquinone and two varying diols namely 3,3'-(1,4-phenylene)bis(1-(4-hydroxyphenyl)prop-2-en-1-one) (THAP) and 3,3'-(1,4-phenylene)bis(1-(4-hydroxy-3-methoxyphenyl)prop-2-en-1-one) (TMAP) and diacid chlorides (succinyl, glutaryl and oxalyl chlorides) were used for the synthesis of copolyesters by solution polycondensation. Acid catalyzed Claisen-Schmidt reaction was employed to synthesize the two varying diols. These photo sensitive copolyesters were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Thermal transitions were recorded from DSC thermograms. Hot stage optical polarized microscopy (HOPM) was utilized to ascertain the liquid crystallinity of these copolyesters. The photocrosslinkability of the copolyesters was established with UV irradiation and SEM analysis.

INTRODUCTION

Polymers containing photosensitive functional groups have attracted considerable attention in the research field. Photochemical reactions may provoke many changes in physiochemical properties such as solubility, dielectric constant, optical transparency and refractive index. [A.Rehab etal 1999, N. Kawatzwki etal, 1999]. Photoresponsive polymers have also acquired potential importance in various industrial applications, such as liquid crystalline display [H.Chen etal, 2004, S.W. Fang etal, 2002], optical wave guide materials [XD. Li etal, 2004, YH. Qi etal, 2006 P. Wen etal, 2011]. Photocrosslinkable polymers have found applications in microlithography including integrated circuit technology, printing technology, photofabrication, photoconductors, photocrosslinked hydrogels etc. [A. Reiser, 1989, E. Gipstein etal, 1970, S. Tazuke 1982, K. Subramanian etal, 2000]. Polymers having photodimerizable groups find applications in immobilization of enzymes [D. Roopsingh etal, 2012]. Chalcone (α,β unsaturated carbonyl) group among various photosensitive groups such as cinnamoyl, thymine and coumarin, is the most widely studied and used, as it shows high photoreactivity and is able to achieve high level of photocrosslinking upon irradiation with UV light even without adding a sensitizer [K. Feng etal, 1998, Priyarega etal, 2003]. In this paper, we report the synthesis, characterization and photocrosslinking property of a series of novel photosensitive random copolyesters.

EXPERIMENTAL SECTION

Aldrich samples of terepthaldehyde, 4-hydroxyacetophenone and 3-methoxy-4-hydroxy acetophenone were used as received. 1,5-dihydroxyanthraquinone was used as received. Aldrich samples of succinyl, glutaryl and oxalyl chloride were purchased and used for the copolymerization process. SD-Fine AR sample of Dimethyl acetamide

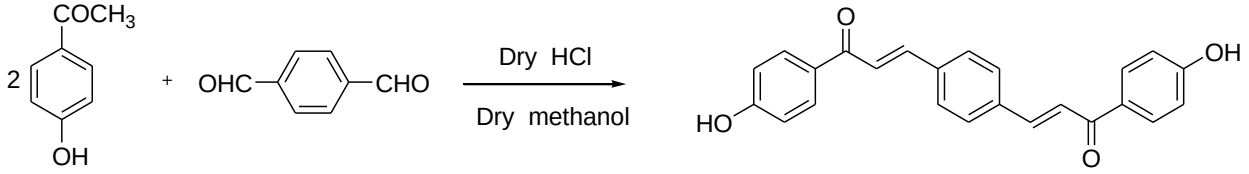
(DMAc) was used as such solvent for finding out the inherent viscosity of the copolyester in solution. Spectral grade DMSO-d_6 (Aldrich) was used as internal standard for recording NMR Spectra.

Synthesis of Chalcone Diol

The monomers 3,3'-(1,4-phenylene)bis(1-(4-hydroxyphenyl)prop-2-en-1-one) (THAP) and 3,3'-(1,4-phenylene) bis(1-(4-hydroxy-3-methoxy phenyl)prop-2-en-1-one) (TMAP) were synthesized by the process reported by Chitra and coworkers [M. Chitra etal, 2013].

Preparation of THAP

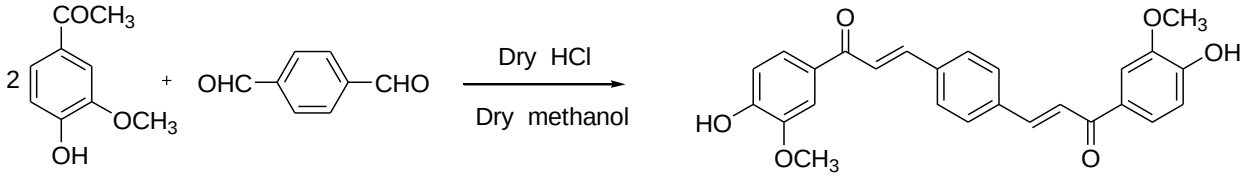
Dry HCl gas was passed through a well-cooled and stirred solution of 4-hydroxyacetophenone (60mmol) and terephthaldehyde (30mmol) in 50mL of dry methanol. Yellow crystals of THAP separated out. It was washed with double-distilled water and re-crystallized from hot methanol. Yield: 90% m.p.: 262–264°C; IR(KBr) 3597 (b, O–H), 1652(s, C=O) cm-1; ^{1}H NMR (DMSO-d6) δ 9.1 (s, 2H, –OH), δ 7.5–8.2 (m, 12H, aromatic), δ 6.7–6.9 (dd, 2H, –CH=CH–) and MS (EI) m/z 370 [M]+.



3,3-(1,4-phenylene)bis(1-(4-hydroxyphenyl)prop-2-en-1-one

Preparation of TMAP

Dry HCl gas was passed through a well-cooled and stirred solution of 4-hydroxy-3-methoxyacetophenone (60mmol) and terephthaldehyde (30mmol) in 50 mL of dry methanol. Yellow crystals of TMAP separated out. It was washed with double-distilled water and re-crystallized from hot methanol. Yield: 85% m.p.: 239°C; IR(KBr) 3508 (b, O–H), 1642(s, C=O) cm^{-1}; ^{1}H NMR (DMSO-d6) δ 9.8 (s, 2H, –OH), δ 7.2–8.3 (m, 7H, aromatic), δ 6.7–6.9 (dd, 2H, –CH=CH–), δ 3.5 (s, 6H, –OCH_3) and MS (EI) m/z 430 [M]+.



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

Synthesis of Copolyesters

The procedure [E. Arumugasamy etal, 2000] for the synthesis of a typical aliphatic diacid-based copolyester is given here.

The monomer THAP (1mmol.) and the diol 1,4-dihydroxyanthraquinone was dissolved in 15ml of DMF in a 100mL round-bottomed flask. After 5 minutes 1mL of triethylamine was added and stirred. The mixture was allowed to stir at room temperature for 15 minutes in inert atmosphere. Then the diacid chlorides succinyl chloride (0.5mmol.) or glutaryl chloride (0.5mmol.) or oxalyl chloride (0.5mmol) was added with constant stirring. Then the temperature was raised to 100°C and maintained at this temperature with continuous stirring for a span of 3 hours. At last the reaction mixture was poured into 100ml of methanol when the copolyester was precipitated. It was filtered, washed with dry methanol and dried in vacuum.

The diacid chlorides, diol-I and diol-II used and the copolyester code of the four copolyesters are represented in Table 1.

RESULTS

Solubility of all the copolyesters was determined in various solvents qualitatively and they were found to be readily soluble in aprotic polar solvents. The inherent viscosity (η_{inh}) of the polyesters was determined in DMAc solution using Ubbelohde viscometer at 30°C. The values ranged from 0.34 to 1.17 which indicates the polymers were of high molecular weight. FT-IR spectra of the entire random copolyesters were recorded using Shimadzu FT-IR instrument. The ^{1}H and ^{13}C-NMR spectra were recorded with BRUKER AV III 500 MHz NMR instrument in DMSO-d6 solvent. DSC thermograms of all the four copolyesters were obtained using DSC 200 F3 MAIA instrument. The copolyesters were subjected to UV irradiation at various time intervals which resulted in the

photocrosslinking of the polymers. SEM studies of the polymer film indicated morphological changes before and after UV irradiation.

Table-1: Monomer diols used and the copolyester code of the six copolyesters together with percentage of yield and inherent viscosities (η_{inh})

Diol-I:1,5-dihydroxy anthraquinone		**Copolyester code**	**Yield (%)**	η_{inh} **(dL/g)**
Diol-II	**Diacid chloride**			
THAP	Succinyl chloride	PSQH	76.31	0.723
TMAP	Succinyl chloride	PSQM	80.46	1.17
THAP	Glutaryl chloride	PGQH	77.76	0.606
TMAP	Glutaryl chloride	PGQM	79.22	0.838
THAP	Oxalyl chloride	POQH	83.86	0.342
TMAP	Oxalyl chloride	POQM	85.44	0.371

Table 2: Solubility of copolyesters in common organic solvents

Copolyester	C_6H_{12}	C_6H_6	$CHCl_3$	**EtOAc**	$(CH_3)_2CO$	CH_3OH	**DMAc**	**DMF**	**DMSO**
PSAH	--	--	+-	+-	+-	--	++	++	++
PSAM	--	--	+-	+-	+-	--	++	++	++
PGAH	--	--	+-	+-	+-	--	++	++	++
PGAM	--	--	+-	+-	+-	--	++	++	++
POAH	--	--	+-	+-	+-	--	++	++	++
POAM	--	--	+-	+-	+-	--	++	++	++

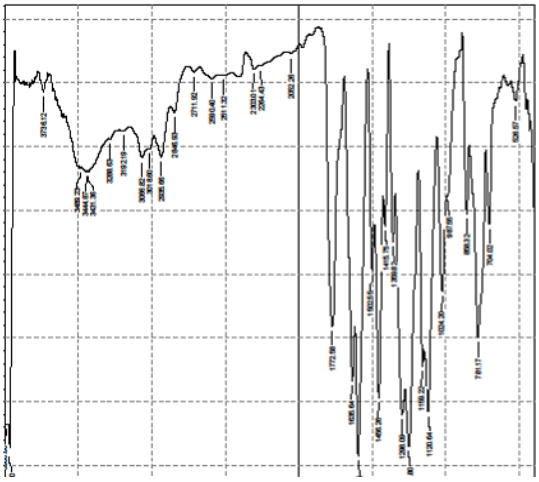
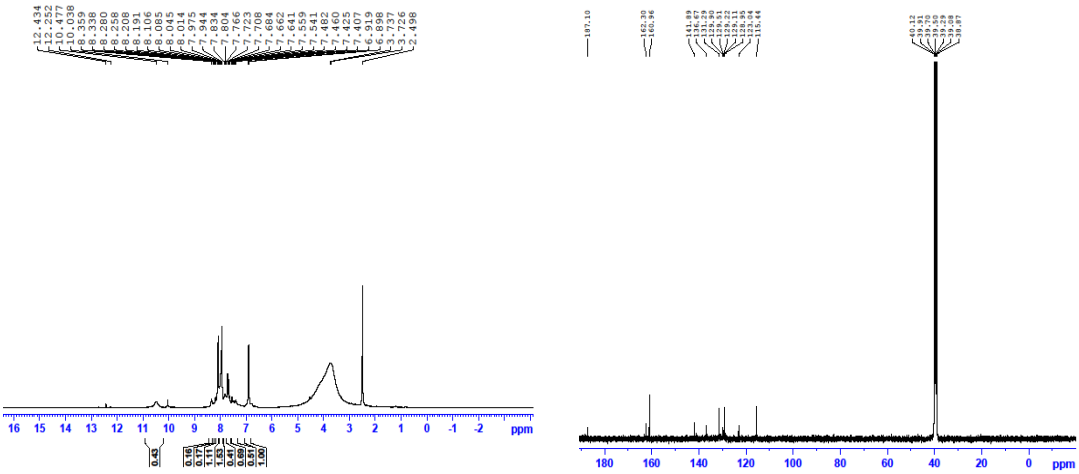


Fig: 1 FT-IR spectrum of POQM



2(a) 2(b)

Fig: 2(a) – ^{1}H-NMR Spectrum of POQH
Fig: 2(b) – ^{13}C-NMR Spectrum of POQH

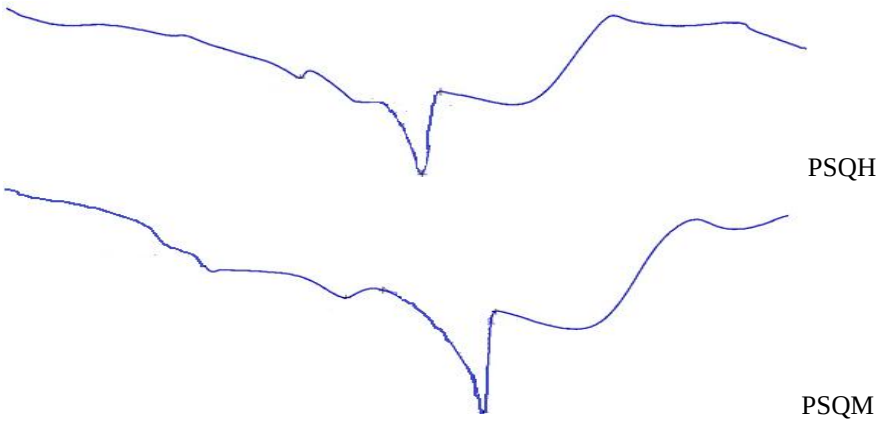
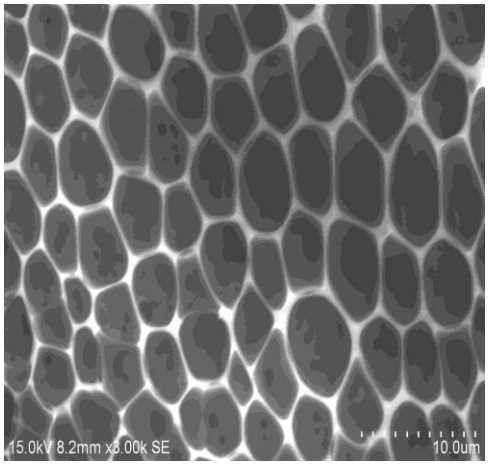
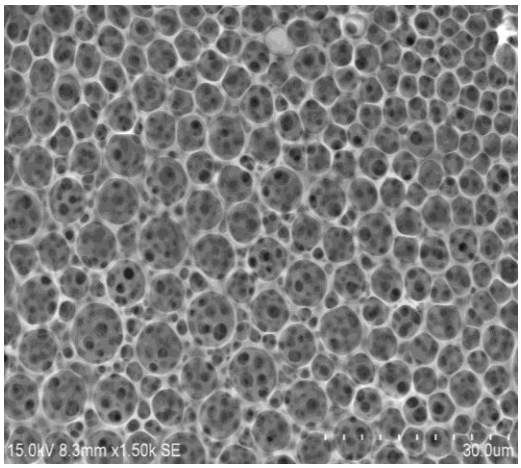


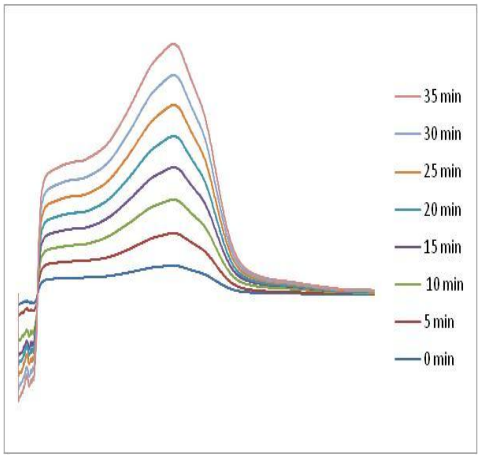
Fig: 3 DSC thermograms of polymers PSQH and PSQM.

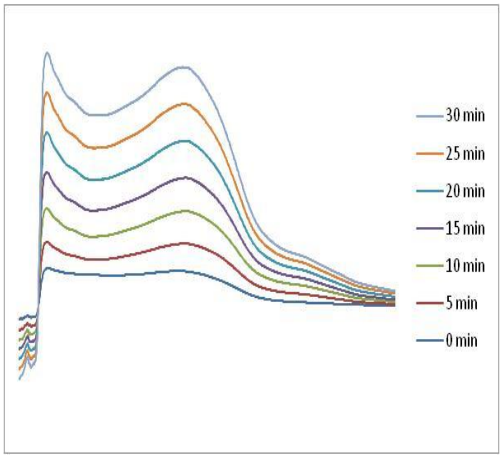




4 a 4b

Fig: 4(a) SEM image of POQM polymer film before exposure to UV radiation
Fig: 4(b) SEM image of POQM polymer film after exposure to UV radiation





5(a) 5(b)

Fig: 5(a) – UV spectrum of PGQH at various time intervals
Fig: 5(b) – UV spectrum of PGQM at various time intervals

DISCUSSION

Solubility

The six copolyesters synthesized here were easily soluble in aprotic polar solvents such as dimethylsulphoxide, dimethylacetamide and dimethylformamide, partially soluble in moderately polar solvents like tetrahydrofuran and acetone but thoroughly insoluble in least polar solvents like benzene and hexane. This might be attributed to the inter-molecular interactions of polar solvents with ester linkage of the polymer molecules. Similar explanation was offered by Sidharthan and coworkers [J. Sidharthan etal, 2012] in a series of copolyester. The results of the solubility of the copolyesters are presented in table 2.

Viscosity Measurements

The inherent viscosity of the resulting copolyesters was determined in dimethyl acetamide solution at 30°C using Ubbelohde viscometer. In each case 25mg of pure dry copolyester sample was dissolved in 25ml of DMAc, kept aside for some time with occasional shaking. The η_{inh} was calculated from the flow time measurements. The inherent viscosity values were found to be in the range of 1.00 - 1.2 dL/g and are presented in table 1. The data shows that these copolyesters are reasonably of high molecular weight.

Spectral Studies

FT-IR spectrum of the six copolyesters was recorded using Shimadzu FT-IR instrument. The FT-IR spectrum of all the six copolyesters showed characteristic absorption in the range of 1757 - 1772cm^{-1} due to ester C=O stretching frequency. Similar observations were made by Perundevi and coworkers [T.S.Perundevi etal, 2014] Samuel and coworkers [S. Samuel etal, 2010] in a series of copolyesters.
The NMR spectra were recorded with BRUKER AV III 500 MHz NMR instrument in DMSO-d6 solvent to identify the structural units present in the copolyester chain. The proton NMR spectrum of POQH is shown in Fig. 2(a). The aromatic protons of chalcones and anthraquinone are observed in the range of 7.4 - 8.35ppm. The vinylic protons attached to the carbonyl carbon are observed in the range of 6.89 - 6.91ppm. The methoxy protons in the chalcone moiety are represented in the range of 3.49 - 3.73ppm. The methylene protons are observed in the range of 2.49 - 3.55ppm. Similar remarks were made Chitra and coworkers [M. Chitra etal, 2010] in a series of copolyesters derived from bischalcones.
The proton-decoupled ^{13}C NMR spectrum of POQH is shown in Fig. 2(b) Chemical shift assignments were made from the off-resonance decoupled spectra of the copolyesters. The ketone carbonyl carbon and ester carbonyl carbon resonance is observed at 187ppm and 172ppm, respectively. The resonance signal at 131ppm arises from other aromatic carbons in the polymer. [Senthamizh Selvi etal, 2012].

Thermal and liquid crystalline properties

DSC thermograms of the six copolyesters were recorded using DSC 200 F3 Maia instrument at a heating rate of 10 K/min in an atmosphere of nitrogen. DSC thermograms reveal the decomposition data of the polymers. The glass transition temperature (T_g), melting temperature (T_m), decomposition temperature (T_d) can be inferred from the thermograms.

Photocrosslinking studies

The photocrosslinking studies were carried out to learn the variations that occurred in the polymer when subjected to UV irradiation to establish the photoresist nature of the polymer. Photo-responsive polymers possessing chalcone moiety in the side chain or in the main chain behave as a negative photoresist subsequent from the photocycloaddition, as it is well known [B.H. Lee etal, 2004]. The polymer solution was prepared in the concentration range of 10-20mg/L using dimethyl acetamide. It was irradiated under 160W mercury lamp and the changes due to UV absorption in the bischalcone based polymers caused by photoreaction were investigated by *in-situ* UV-Vis absorption spectroscopy. Both trans-cis isomerization and dimerization of chalcone are anticipated upon exposure of the polymers to UV irradiation.
The unimolecular isomerization arises through a rotation mechanism from the trans-to the cis-form when the UV light has excited the π electrons of the carbon-carbon double bond. The dimerization, which is a bimolecular reaction, results in a cross linking of the polymer with formation of cyclobutane rings through a [2+2] cycloaddition of the carbon-carbon double bond. For the polymers in solution the chalcone moiety exhibits an absorption maximum which is ascribed to the π-π^* transitions through the chalcone system for the trans-isomer.
The intensity of this absorption decreases fast upon exposure to UV light which specifies the disruption of conjugation, either due to dimerization or trans-cis isomerization. All the polymers synthesized exhibits photocrosslinkability. The absorption band around 360–400nm is due to π-π^* transition of the exocyclic double bond of the bischalcone unit in the polymer. As the time of irradiation increases there is a decrease in absorbance which indicates the steady rate of photocrosslinking. The reason behind this is the photodimerization of C=C bonds in the chalcone moiety, which engages $2\pi+2\pi$ cycloaddition reactions leading to the formation of cyclobutane ring.
To compare the relative reactivity of these polymers a plot of (A_0-A_t/A_0) against time was obtained, where A_0 is the absorbance before irradiation and A_t is the absorbance after irradiation for time t.

It is significant from these plots that the rate of cross-linking increases steeply with time of irradiation initially (up to 10 minutes) and after this period there is a linear increase with time of irradiation

Morphological study by SEM

The synthesized copolyesters contains bischalcone moiety, which functions as the photo-active chromophore. About 10mg of the finely powdered copolyester and 90mg of PVC were dissolved in THF and stirred continuously for 5 minutes. Then the polymer blend was poured on a thin glass plate and dried to form a thin and even polymer film. The morphology of the polymer film was studied and then it was exposed to UV irradiation for 30 minutes and subjected to SEM. The SEM images of the polymer films before and after irradiation to UV light illustrates the changes in the morphology. The change in the surface of the film before and after irradiation of UV light is due to photocrosslinking.

CONCLUSION

The research study reports the synthesis of copolyesters by direct polycondensation method. Viscosity measurements reveal that the polymers synthesized are of high molecular weight. The synthesized polymers have been characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR spectral studies. The structural assignment of the polymers is supported by these spectral data. The liquid crystalline property of the polymers was recognized from DSC and confirmed by HOPM images. The photocrosslinking study of the polymers reveals their requisite importance in photoresist applications. Hence the polymers synthesized shows photoresponsiveness as well as liquid crystalline property, and they might be valid in non linear optical applications and optical data recording.

ACKNOWLEDGMENT
We express our gratitude to the Instrumentation Centre of Ethiraj College for Women, Chennai for providing spectral data.

REFERENCES

1. Arumugasamy, E., Baskar, B. and Kannappan, V. (2000): Synthesis and characterization of certain thermotrophic liquid crystalline random copolyesters. J. Pol. Mat. 17: 4-9
2. Chen, H. and Yin, J. (2004): Synthesis and characterization of negative-type photosensitive hyperbranched polyimides with excellent organosolubility from an A2 + B3 monomer system. J. Polym. Sci., Part A: Polym. Chem., 42(7): 1735-1744.
3. Chitra, M., Rajendran, T.V., Duraipandiyan, V., Rajan, Y.C. and Reuben Jonathan, D. (2010): A study on the synthesis and bactericidal activity of certain copolyesters containing bischalcone moiety in the main chain. Ind. J. Sci. Tech. 3(8): 890-893.
4. Chitra, M., Reuben Jonathan, D., Rajan, Y.C. and Duraipandiyan, V. (2013): A Study on the Synthesis and Antibacterial Evaluation of Certain Copolyesters Containing Bischalcone Moiety in the Main Chain. Int. J. Chem. Appl. 5(2): 73-81.
5. Fang, S.W., Timpe, H.J. and Gandini, A. (2002): Photocrosslinkable polymers bearing pendant conjugated heterocyclic chromophores. Polymer, 43(12): 3505-3510.
6. Feng, K., Tsushima, M., Matsumoto, T. and Kurosaki, T. (1998): Synthesis and properties of novel photosensitive polyimides containing chalcone moiety in the main chain. J. Polym. Sci., Part A: Poly. Chem., 36(5): 685-693.
7. Gipstein, E., Hewett, W.A. and Need, O.U. (1970): Synthesis of homologous monomers and polymers of carbazole, phenothiazine and dibenzazepine. J.Polym Sci Part A-1., 8(11): 3285-3294.
8. Kawatsuki, N., Yamamoto, T. and Ono, H. (1999): Photoinduced alignment control of photoreactive side-chain polymer liquid crystal by linearly polarized UV light. Appl. Phys. Lett., 74: 935-937.
9. Li, X.D., Zhong Z.X., Kim, J.J. and Lee M.H. (2004): Novel Photosensitive Fluorinated Poly(arylene ether) Having Zero Birefringence. Macromol. Rapid. Commun. 25(11): 1090-1094.

10. Perundevi, T.S., Reuben Jonathan, D. and Kothai, S. (2014): Synthesis, Characterization and Antibacterial Study of certain Copolyesters containing Bischalcone moiety in the Main chain. Int. J. of Pharm. And BioSci., 5(4): 528-533.
11. Priya rega, S., Muthusamy, A., Kaniappan, K. and Murugavel, S.C. (2003): Synthesis and characterisation of photosensitive polyesters by phase transfer catalysed polycondensation. Des. Mono. & Poly., 6(2): 187-196.
12. Qi, Y.H., Ding, J.F., Day, M., Jiang, J. and Callender, C.L. (2006): Cross-linkable highly halogenated poly(arylene ether ketone/sulfone)s with tunable refractive index: Synthesis, characterization and optical properties. Polymer, 47(25): 8263-8271.
13. Rehab, A. and Salahuddin, N. (1999): Photocrosslinked polymers based on pendant extended chalcone as photoreactive moieties. Polymer, 40(9): 2197-2207.
14. Reiser A. Photoreactive polymers- the science and technology of resist. New York: Wiley, 1989.
15. Roop Singh, D., Vasanthi, S. and Arulmoli, J. (2012): Synthesis of Certain Poly[bis(benzylidene)] Esters and Investigation on their Photocrosslinkability. E.J of Chem., 9(1): 145-148.
16. Senthamizh Selvi, R., Nanthini, R. and Sukanyaa, G. (2012): Synthesis and Characterisation of two random copolyesters by Phase-transfer catalyst polycondensation. Int. J. of Sci. and Tech. Res. 1(1): 1-3.
17. Sidharthan, J., Reuben Jonathan, D. and Peter Amaladhas T. (2012): Synthesis and Characterization of Certain Thermotropic Liquid Crystalline Copolyesters Containing α,β-Unsaturated Ketone in the Main Chain. Int. J. Chem. Appl. 4(3): 241-250
18. Subramanian, K., Krishnasamy, V., Nanjundan S. and Rami Reddy A.V. (2000): Photosensitive polymer: synthesis, characterization and properties of a polymer having pendant photocrosslinkable group. Eur. Poly. J. 36(11):2343-2350.
19. Sugaraj Samuel, R., Reuben Jonathan, D., Christurajan, Y., Jayakumar, S. and Pichai, R. (2010): Synthesis, Characterization and Ultrasonic Determination of Certain Copolyesters Containing Bis(Arylidene)Acetone Moiety in the Main Chain. Ind. J. Sci. Tech. 3(6): 696-701.
20. Tazuke, S. Developments in polymer photochemistry, vol. 3. London: Applied Science Publishers, 1982.
21. Wen, P., Wang, L., Zhang, A., Li, XD. and Lee, MH. (2011): Synthesis and properties of novel photosensitive poly(arylene ether sulfone) containing chalcone moiety in the main chain. Mat. Chem. Phy. 126(3): 832-835.