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Synthesis, characterization and thermal stability of poly (azomethine) esters containing different linkage groups

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ABSTRACT

This paper describes the synthesis of polyesters with azomethine groups by the reaction of dihydroxy monomers with other linkage groups (-PO- / -S-) between phenylene rings with diacids [naphthalene 2,6-dicarboxylic acid (NDA), cyclobutane1,2-dicarboxylic acid (CDA) and 3,3'-bisphenyldicarboxylic acid (BDA)] have been prepared. The characterization of synthesized polyesters was done by using FTIR and ^{1}H-NMR spectroscopic techniques. Their thermal stability has been studied by thermogravimetric analysis.

KEYWORDS

Azomethine;
Polyester;
Thermal stability.

INTRODUCTION

When rigid, rod shaped molecules (mesogens) are present as a part of the polymer backbone, it is anticipated to give liquid crystal behaviour[1-3]. Owing to the very high melting point, the aromatic backbone are segmented with spacers. The spacer is usually a sequence of methylene units. Moreover, when chromophoric groups such as azo, azomethine are present in such polymers, they influence the thermal and liquid crystalline behaviour[4,5]. In this report, the synthesis, characterization and thermal stability of new polyesters with azomethine groups by reacting the dihydroxy monomers containing azomethine groups with aromatic diacid chlorides. There are only a few reports about the polymers with azomethine groups as mesogens[6,7]. The azomethine polymers derived from aliphatic diacid chlorides are expected to show liquid crystalline properties. Those derived from aromatic diacid chlorides do not melt before degradation. Hence, their liquid crystalline properties cannot be assessed.

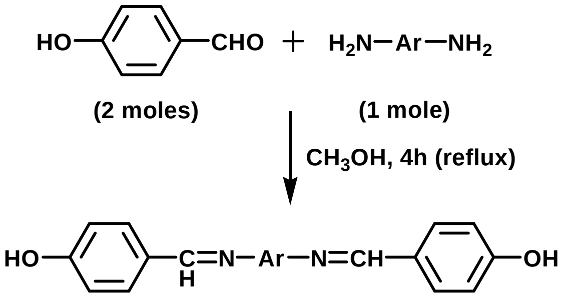
EXPERIMENTAL

Materials

4-hydroxybenzaldehyde (H), 4,4'-diaminodiphenyl sulfone (DDS), 4,4'-thiodianiline (TDA), naphthalene 2,6-dicarboxylic acid (NDA), cyclobutane1,2-dicarboxylic acid (CDA) and 3,3'-bisphenyldicarboxylic acid (BDA) were purchased from Aldrich and used as received. Methanol, sodium hydroxide, thionyl chloride, N-methyl pyrrolidone, pyridine and dioxin (CDH) were used as such. Bis (3-aminophenyl) methylphosphine oxide (BAP) and bis (3-aminophenyl) phenylphosphine oxide (BAPP) were synthesized in our laboratory according to the reported methods[8,9].

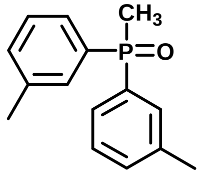
Synthesis of dihydroxy monomers with azomethine

Dihydroxy monomers with azomethine groups were synthesized by the following reaction Scheme 1:

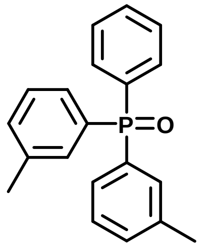


Scheme 1 : Synthesis of dihydroxy monomer

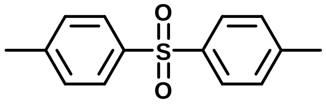
where Ar is



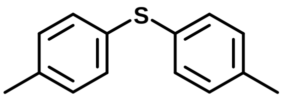
bis(3-aminophenyl)methylphosphine oxide(BAP)



bis(3-aminophenyl)phenylphosphine oxide (BAPP)



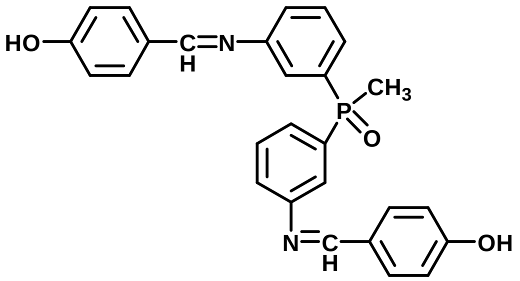
4,4'-diaminodiphenyl sulfone (DDS)



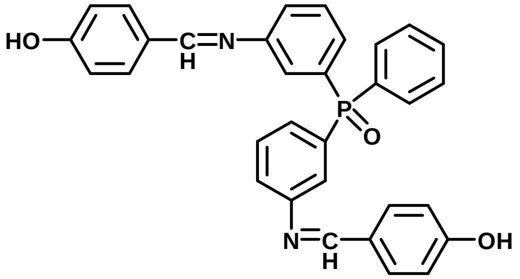
4,4'-thiodianiline (TDA)

A mixture of 4-hydroxybenzaldehyde (H) (0.1mole) and 4, 4'-diaminodiphenyl sulfone (DDS) (0.05mole) was refluxed in methanol for 4hours. Then the reaction mixture was then cooled and the resulting solid was recrystallized from dioxin to give dihydroxy monomer having azomethine groups.

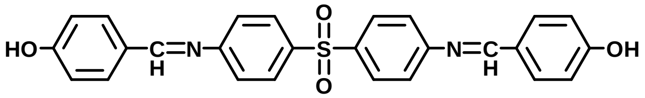
Similarly, the other azomethine dihydroxy monomers were prepared from 4-hydroxybenzaldehyde (H) and diamines TDA/ BAP/ BAPP. The structure of azomethine as follows:



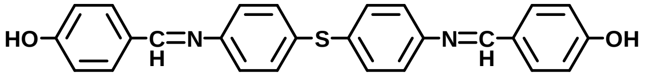
(1)



(2)



(3)



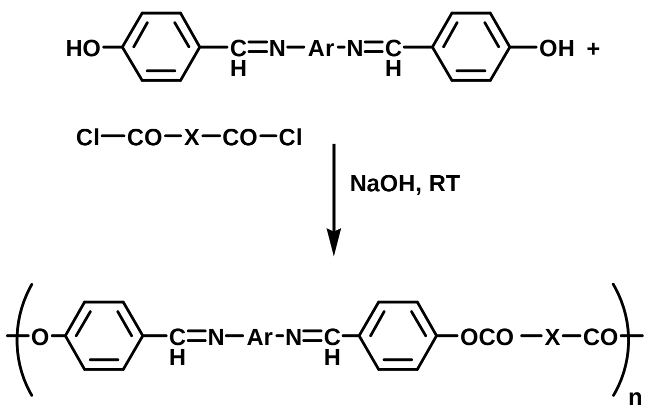
(4)

Structure of Dihydroxy monomer

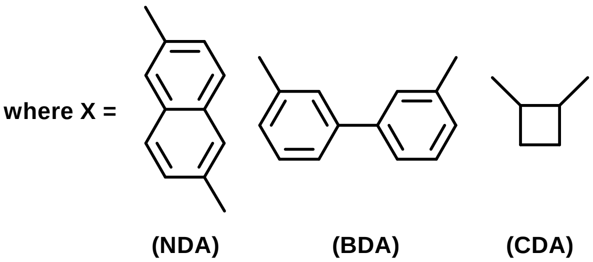
Synthesis of polyesters with azomethine groups

The dihydroxy monomers (synthesized according to the reaction Scheme 1) were condensed with diacid chloride to give polyesters (Scheme 2). The three different diacid chloride were prepared from the respective diacids naphthalene 2, 6-dicarboxylic acid (NDA), cyclobutane1, 2-dicarboxylic acid (CDA) and 3, 3'-bisphenyldicarboxylic acid (BDA) by treatment with thionyl chloride.

The polyester was prepared using the following procedure: 1 mmol of diacid (NDA/ BDA/ CDA) was dissolved in 5 mL of N-methyl pyrrolidone in a dry 3-necked flask. The solution was cooled to –10°C and 0.298 g (2.5 mmol) of thionyl chloride was added, followed by stirring for 2 min. Then 1 mmol of dihydroxy monomer and pyridine 0.198 g (2.5 mmol) were added



Scheme 2 : Synthesis of polyesters



to the mixture. It was stirred for 15 h at 0°C and then for 2 h at room temperature. Then the viscous reaction mixture was added to 25 mL of methanol. The precipitated polymer was collected by filtration and was dried at 80°C for 8 h under vacuum to leave a brown solid.

Furthermore, other polyesters were prepared by the above procedure.

Characterization

The dihydroxy monomers were characterized by elemental analysis. IR spectra of these monomers (1/2/3/4) and polyesters in KBr pellets were recorded using a Biorad Digilab FTS-40 FTIRspectrometer. ^{1}H-NMR spectra were recorded on a Bruker AC 300 spectrometer at a frequency of 300 MHz using DMSO-d6 as solvent and tetramethyl silane as an internal standard.

Thermal stability

Thermal stability of the cured resin in nitrogen atmosphere (flow rate 60 cm3/min) was evaluated using a Du Pont 2100 thermal analyser having a 951 TG module. A sample weight of 10 ±2 mg and a heating rate of 20°C/min was used.

RESULTS AND DISCUSSION

Structural characterization

The elemental analysis values of the resulting dihydroxy monomers were in good agreement with the calculated values for the proposed structures (TABLE 1).

TABLE 1 : Results of C, H, and N elemental analysis

Sample designation	Molecular formula	(%) C	H	N
1	$C_{27}H_{23}N_2O_3P$	70.8(71.5)	4.9(5.0)	6.0(6.2)
2	$C_{32}H_{25}N_2O_3P$	73.9(74.6)	4.7(4.9)	5.3(5.4)
3	$C_{26}H_{20}N_2O_4S$	68.1(68.4)	4.1(4.4)	5.9(6.1)
4	$C_{26}H_{20}N_2O_2S$	73.4(73.6)	4.5(4.7)	6.3(6.6)

Numerical values within parenthesis represent the calculated values.

All the polyesters are soluble in conc.H_2SO_4 and polyesters obtained from aromatic acid chlorides are partially soluble in o-chlorophenol. However, polyesters obtained from aliphatic diacids are soluble in all three solvents. (TABLE 2)

TABLE 2 : Properties of polymers

Sample designation	Yield (%)	Solubility test DMF	Conc.H_2SO_4	o-chlorophenol
1 + NDA	74.1	+_	++	+-
2 + NDA	61.0	--	++	--
3 + NDA	64.7	++	++	+-
4 + NDA	91.0	++	++	+-
1 + BDA	73.0	+-	++	+-
2 + BDA	54.5	+-	++	+-
3 + BDA	84.9	++	++	+-
4 + BDA	82.0	++	++	+-
1 + CDA	67.6	++	++	++
2 + CDA	51.0	++	++	++
3 + CDA	62.0	++	++	++
4 + CDA	92.0	++	++	++

(++) = soluble, (+-) = partially soluble, (—) = insoluble

The IR spectra contain C=N stretch at 1610-1630cm^{-1}. Bands at about 3500-3600 cm^{-1} were observed of monomers (1/ 2/ 3/ 4) due to stretching vibrations of OH group. A sharp peak at 1735-1740 cm^{-1} of polyesters is due to the ester link[10,11] (which is not observed in the monomer). The broad peak around 1580-1660 cm^{-1} implies the C=C stretch in benzene ring.

In ^{1}H-NMR spectra of dihydroxy monomers, a signal due to hydroxyl proton was observed at δ 5.6 ± 0.5ppm, CH=N proton of azomethine group at 8.3 ± 0.3 ppm and a multiplet due to aromatic protons was observed in the range of δ = 6.5-8.0 ppm (TABLE 3). The P-CH_3 was also observed at δ =3.3 ppm in the case of (1). The integration was used to calculate the number of protons.

TABLE 3 : Results of ^{1}H-NMR spectra along with their assignment

Sample Desigantion	CH=N (ppm)	CH_3 (ppm)	Ar (ppm)	OH (ppm)
1	8.1(2H)	3.3 (3H)	6.5-7.8 (16H)	5.6 (2H)
2	8.4(2H)	-	6.6-8.0(21H)	5.5 (2H)
3	8.3(2H)	-	6.5-7.5 (16H)	5.7 (2H)
4	8.5(2H)	-	6.5-7.9 (16H)	5.5 (2H)

In ^{1}H-NMR spectra of polyesters, a signal due to (CH=N) proton of azomethine group at 8.1± 0.4ppm and multiplets due to aromatic protons (6.7-8.2 ppm).

Thermal stability

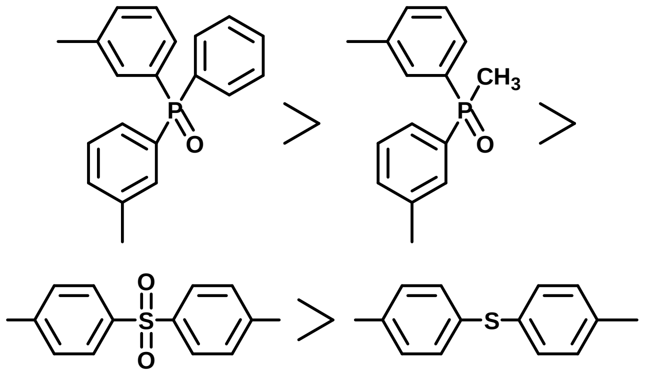
The TG curves of the polyazomethine esters from NDA, BDA and CDA chlorides were recorded. The temperatures corresponding to 10 and 20% weight-loss of the polymers on thermal degradation are summarized in TABLE 4.

TABLE 4 : TG data for the polyesters*

Sample designation	$T_{(10\%)}$ °C	$T_{(20\%)}$ °C
1 + NDA	440	512
2 + NDA	444	484
3 + NDA	460	500
4 + NDA	324	460
1 + BDA	424	472
2 + BDA	466	532
3 + BDA	356	440
4 + BDA	312	404
1 + CDA	372	396
2 + CDA	348	432
3 + CDA	300	432
4 + CDA	216	312

***$T_{10\%}$ = Temperature of 10% weight-loss; $T_{20\%}$ = Temperature of 20% weight-loss.**

Thermogravimetric analysis indicates that, for fully aromatic polyesters, the NDA and BDA polyesters have thermal stability higher than the polyesters derived from the aliphatic acid chlorides (CDA). Among the aromatic azomethine polyesters, due to the higher stability of ester group attached to aromatic ring[12] as well as the aromatic azomethine group, the probable chain scission is at the bridge between phenylene rings. For 20% degradation, the order of stability for polyesters 1+NDA and 2+NDA as well as 1+BDA and 2+BDA is found to be



Thermal stability of naphthalyl polyesters is slightly higher than the bisphenyl polyesters. However, polyazomethine esters from the aliphatic acid show a different type of thermal stability because degradation in their cases leads to ester scission[13]. Taking into consideration the structure of bisphenols, it may be observed that the polyesters from the bisphenol 2 exhibit a higher thermal stability which is comparable to that of the polyesters derived from bisphenol 4. Naphthalic and bisphenyl polyesters do not melt before decomposition.

CONCLUSIONS

These polyesters showed good solubility and thermal stability characterized by thermal gravimetric analysis (TGA). The introduction of phosphine oxide moiety into the backbone of the polymer increased thermal stability than sulphur moiety. These properties can make this polymer attractive for practical applications.

REFERENCES

[1] 'Liquid Crystallinity in Polymers', A.Ciferri, (Ed); VCH Publishers, New York, **(1991)**.

[2] K.N.Sivaramakrishan, A.Blumstein, S.B.Clough, B.Blumstein; Polym.Prepr.(ACS), **19**, 190 **(1978)**.

[3] **(a)** D.Sek; Eur.Polym.J., **20**, 805 **(1984)**; **(b)** Ogiri, M.Ikeda, A.Kanazawa, T.Shiono, T.Ikeda; Polymer, **(1999)**; **(c)** C.Rangaswamy, L.Ravikumar, K.Ramarajan; J.Indian Chem.Soc., **69**, 788 **(1992)**.

[4] L.Ravikumar, M.B.Prasad, B.J.Vasanthi; Materials Chemistry and Physics, **115(2-3)**, 632 **(2009)**.

[5] I.Kaya, S.Koyuncu, S.Culhaoglu; Polymer, **49(3)**, 703 **(2008)**.

[6] S.C.Ryu, Y.C.Jeong, L.S.Park; Mol.Crystals and Liquid Crystals, **514**, 565 **(2009)**.

[7] A.Muthuswamy, S.Karthikeyan, K.Ramarajan, L.Ravikumar; J.Indian Chem.Soc., **78**, 23 **(2001)**.

[8] P.Khurana, S.Aggarwal, A.K.Narula, V.Choudhary; J.Appl.Polym.Sci., **87**, 1345 **(2003)**.

[9] Y.L.Liu, G.H.Hsiue, R.H.Lee, Y.S.Chiu; J.Appl. Polym.Sci., **63**, 895 **(1997)**.

[10] R.Mani, C.Rangaswamy, K.Ramarajan, L.Ravikumar; Makromol.Chem.Rapid Commun., **9**, 417 **(1988)**.

[11] 'The Infrared Spectra of Complex Molecules', L.J.Bellamy, (Ed); Chapman Hall, London, **2**, **(1980)**.

[12] H.J.Hagemeyer; US Pat. 3043808, **(1962)**.

[13] **(a)** E.F.Izard; J.Polym.Sci., **9**, 35 **(1952)**; **(b)** H.A.J.Schoutissen; J.Am.Chem.Soc., **55**, 4535 **(1933)**.