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Mesomorphic Polymers-IV: Synthesis, Characterization and Evaluation of Mesogenic and other Physical Properties of Polyesters and Polyamides Obtained from 1,2-Bis (4′-Carboxy-Phenoxy) Ethane

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MESOMORPHIC POLYMERS-IV: SYNTHESIS, CHARACTERIZATION AND EVALUATION OF MESOGENIC AND OTHER PHYSICAL PROPERTIES OF POLYESTERS AND POLYAMIDES OBTAINED FROM 1,2-BIS(4'-CARBOXY-PHENOXY)ETHANE

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Eleven polyesters and polyamides are synthesized by polycondensation of diacid chloride of 1,2-bis(4'-carboxy-phenoxy)ethane with different dihydroxy compounds and diamines. All the polyesters exhibit mesomorphism. Aliphatic-aromatic polyamides are mesogenic whereas, aromatic polyamides are non-mesogenic. Polymers are characterized by elemental analysis and IR spectra. The viscosity of soluble polymers is measured. The effect of chemical constitution and viscosity on mesomorphism is evaluated. One branched chain polyester exhibits nematic mesophase at room temperature and is quite stable with a long mesophase range. The thermogravimetric analysis is carried out to evaluate the thermal stability of one of the samples.

1. INTRODUCTION

Number of new polymers are being reported which exhibit liquid crystalline properties as they are of both theoritical and commercial interest. Recently, the technological applications and possibility of large structural variations have given impetus for the synthesis of mesogenic condensation polymers.

Griffin and Havens[1] evaluated the effect of flexible spacers of different length on mesomorphism by synthesizing polyesters having flexible spacers both in acid and phenolic monomers. In the present study it was proposed to synthesize polyesters and polyamides having a fixed flexible spacer in one monomer to evaluate the effect of other parameters on the mesogenic character of resultant polymers.

With this in view eleven polyesters and polyamides are synthesized by using 1,2-bis(4'-carboxy-phenoxy)ethane as one of the monomers.

2. EXPERIMENTAL

2.1 Preparation of 1,2-bis(4'-carboxy-phenoxy) ethane

This was prepared by the known method[1,2]. The melting point tellies with the literature (352 °C).

2.2 Preparation of diacid chloride of 1,2-bis-(4'-carboxy-phenoxy)ethane

Diacid chloride of 1,2-bis(4'-carboxy-phenoxy)-ethane was prepared by reacting acid with

thionyl chloride (2.5 mol)and heating on water bath till the evaluation of hydrochloric acid ceased. One to two drops of dry pyridine was used in the reaction as catalyst. Excess of thionyl chloride was distilled off under reduced pressure using a water pump and the diacid chloride left behind as a residue was used in next reaction without further purification.

2.3 Preparation of polyesters

Diacid chloride of 1,2-bis(4'-carboxy-phenoxy) ethane (BCPE) was condensed with different dihydroxy monomers.

$$Cl\text{-}CO\text{-}C_6H_4\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C_6H_4\text{-}CO\text{-}Cl \quad + \quad \underset{\text{BCPE}}{}$$

$$HO\text{-}R\text{-}OH \longrightarrow$$

dihydroxy compound

$$\left[OC\text{-}C_6H_4\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C_6H_4\text{-}COO\text{-}R\text{-}O\right]_n$$

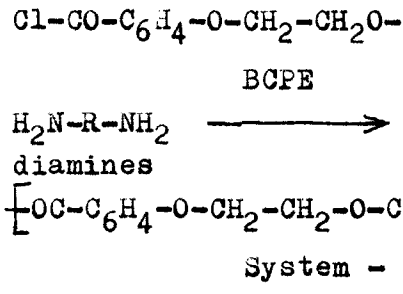
System - I

Respective dihydroxy monomer (0.01 mol) was dissolved in dry pyridine (5 ml) and was added slowly in a quickfit 50 ml round bottom flask containing magnetic niddle and a solution of diacid chloride of 1,2-bis(4'-carboxy-phenoxy)-ethane in dry pyridine (10 ml) with stirring in a cold condition keeping the flask in ice bath. The reaction mixture was stirred continuously with guard tube on the flask and temperature was allowed to rise to room temperature (23°C) then it was stirred further for six hours. At the end of six hours the whole mass was acidified with

cold 1:1 hydrochloric acid. The solid product was filtered, washed with dilute hydrochloric acid followed by washing of water for the complete removal of mineral acid. The product was washed with DMF twice followed by alcohol to remove unreacted material and to get pure polymeric material. The solid polymer was dried and melting point and transition temperatures were determined. The data of all the polymers is recorded in Table 1.

2.4 Preparation of polyamides

Diacid chloride of BCPE was condensed with different diamines.



System - II

Respective diamine monomer (0.01 mol) was dissolved in dry pyridine (5 ml) and was added slowly in a quickfit 50 ml round bottom flask containing magnetic niddle and a solution of diacid chloride (0.01 mol) of 1,2-bis(4'-carboxy -phenoxy)ethane in dry pyridine (10 ml) with stirring in cold condition keeping the flask in ice bath. The reaction mixture was stirred continuously with guard tube on the flask for one and a half hour by maintaining the tempera-

ture between 0 to 5°C. After the stirring period was over, the whole mass was acidified with cold 1:1 hydrochloric acid. The solid product was filtered, washed with dilute hydrochloric acid followed by washing of water for complete removal of mineral acid. The product was washed with DMF twice followed by alcohol to remove unreacted material and to get pure polymeric material. The solid polymer was dried and melting point and transition temperatures were determined. The data of all the polyamides is recorded in Table 1.

2.5 Characterization of polymer samples

2.5.1 Elemental Analysis: The elemental analysis of all the polymer samples is satisfactory.

2.5.2 IR spectra: All the polymers were screened by using KBr pellets in the range of infrared frequency. The data of two polyesters and two polyamides is given in Table 2.

2.6 Transition Temperature Measurements

A polarizing microscope provided with mettler FP-2 heating stage was used to observe mesomorphism in the polymer samples. The mesomorphic properties are recorded in Table 1.

2.7 Viscosity Measurements

The polymer samples which were soluble in suitable solvents were dissolved and their solution viscosity was measured.

Viscosity was measured by taking 0.5%

solution of polymers in DMSO at 30°C by using Ubbelohde viscometer. Intrinsic viscosity $[\eta]$ is calculated by using formula given in the literature[3]. Viscosity data is recorded in Table 1.

2.8 T G A Study

One of the sample is studied by using thermogravimetric analysis method. The percentage weight loss is plotted against the temperature

2.9 Characterization of mesophases by contact method

To characterize and ascertain about the smectic and nematic mesophases of the polymer samples, following low molecular weight mesogens were synthesized.

1. Methyl 4-(4'-n-octadecyloxy-benzoyloxy)-benzylidene-4"-aminobenzoate.
   K $\xrightarrow{102°C}$ S $\xrightarrow{213°C}$ I
2. Methyl 4-(4'-n-hexyloxy-benzoyloxy)benzylidene-4"-aminobenzoate.
   K $\xrightarrow{150°C}$ S $\xrightarrow{214.5°C}$ N $\xrightarrow{272°C}$ I
3. 4(4'-n-propoxy-benzoyloxy)-3-methoxybenzylidene-4"-anisidine.
   K $\xrightarrow{135°C}$ N $\xrightarrow{191°C}$ I

The above smectogen, polymesogen and nematogen are miscible continuously with the polymers exhibiting smectic, polymesogenic and nematic phases.

3. RESULTS AND DISCUSSION

Reference to Table 1 shows that out of eleven polymers, eight polymers exhibit mesomorphism. All the five polyesters are mesogenic in nature whereas out of all polyamides, polyamides with aliphatic spacer groups exhibit mesomorphism. The polyamides having aromatic diamines do not melt upto 325°C hence it could not be ascertained whether they are mesogenic or not.

The polyester BE-1 exhibits only smectic mesophase whereas polyester BE-3 exhibits polymesogenic character. Polyesters BE-2, 4 and 5 exhibit only nematic mesophase. It is interesting to note that even though phenolphthalein and Bisphenol-A will broaden the molecule due to their bulkiness and steric effect, the mesogenic properties are observed in the polymers BE-4 and BE-5. The branching in the polyester BE-2 has brought down the mesogenic temperature upto room temperature. The smectic and nematic mesophases of all these polyesters are characterized by using contact method and known samples as mentioned in the experimental section.

The reference to mesogenic—isotropic temperature clearly shows that phenyl ring (BE-3) enhances thermal stability much more than any other moiety. Polyesters BE-1 and 2 have aliphatic flexible chain, naturally one would expect lowering of mesomorphism[4]. In the case of polyesters BE-4 and 5 though overall polarizability of monomer unit will be more compared to

hydroquinone monomer, due to the increase in breadth and steric hindrance, mesogenic thermal stabilities will decrease. This indicates that the factors which lower the mesogenic thermal stabilities in low molecular weight liquid crystals are operative in these polymers[4].

Polyamides having aliphatic diamines as monomers exhibit nematic mesophases whereas aromatic diamines raise the melting point beyond the limit of microscope. It would be interesting to observe these polyamides (BEA-4-6) at higher temperature under microscope having higher range (upto 500°C) whether they exhibit mesomorphism or not. Polyamide BEA-4 has also a flexible spacer eventhen melting point is $> 325°C$.

These results indicate that all the polyesters exhibit mesomorphism whereas polyamides are relatively high melting. In earlier study[5] we have reported mesogenic ester-amides which exhibit higher thermal stabilities compared to ester linkages in similar compounds. The higher thermal stabilities of these low molecular weight compounds are atributed to the linear structure of polyamide and higher polarizability compared to ester linkage. This explains the high melting behaviour and non-mesomorphism of polyamides having aromatic moiety.

To understand the role of ester linkage and amide linkage on mesomorphism some model compounds were synthesized. It was very interesting to note that model esters were mesogenic

whereas model amides were non-mesogenic and had relatively higher melting points.

In previous study[6] in homopolyesters it was observed that increase in viscosity resulted from smectic to nematic characters and finally at higherviscosity samples did not exhibit mesomorphism. In the present study the polyesters BE-4 and 5 have higher viscosity and exhibit nematic phases. However, in present study no such correlation can be established as the chemical structures of monomers differ in different polyesters. However, in the case of polyamides, synthesis was tried by varying condensation hours to obtain polymers having different degree of polymerization to evaluate the effect of viscosity on mesomorphism but without success as other samples prepared were insoluble in most of the solvents and were infusible upto 325°C.

One of the polyesters BE-3 was studied for its thermal stability using TGA technique. A graph was drawn by plotting the percentage weight loss against the temperature. The sample exhibits good thermal stability. 10% weight loss is at 300°C and 25% weight loss is at 400°C.

CONCLUSIONS

1. Out of eleven polymers, eight polymers exhibit mesomorphism.
2. Branching or deviation from linearity by

TABLE 1 Physical data of polymers

Sr. No.	Code No.	Dihydroxy/ Diamine compound	Transition Temperature(°C)			Viscosity
			S	N	I	$[\eta]$
1	2	3	4	5	6	7
1.	BE-1	Ethylene glycol	101	-	174	0.1009
2.	BE-2	1-Methyl propylene glycol	-	31	203	0.0862
3.	BE-3	Hydro-quinone	215	261	325	-
4.	BE-4	Phenolph-thalein	-	147	194	0.2451
5.	BE-5	Bisphenol-A	-	136	188	0.3392
6.	BEA-1	1,2-Diamino ethane	-	160	288	0.0803
7.	BEA-2	1,3-Diamoni propane	-	138	281	0.1012
8.	BEA-3	1,6-Diamino hexane	-	(275)*	280	-
9.	BEA-4	4,4'-Diamino diphenyl ethane	-	-	325	-
10.	BEA-5	p-phenylene diamine	-	-	325	-
11.	BEA-6	Benzidine	-	-	325	-

* Mesophase observed during cooling .

increase in breadth or steric hindrance lowers solid—mesogenic temperature as well as mesogenic—isotropic transition.

3. One of the polyesters exhibit nematic phase at room temperature which can be utilized for application purposes in optical displays. Two polyesters having good viscosity can find applications for the development of new plastic materials.
4. Polyamides having aromatic moiety raize the melting point beyond 325°C and may be non-mesogenic.
5. TGA study of one polyester BE-3 shows good thermal stability.

TABLE 2 IR Spectral Data

IR Stretching Vibrations

BE-1	BE-3	BEA-3	BEA-5
2940 cm^{-1}	2900 cm^{-1}	3300 cm^{-1}	3310 cm^{-1}
1700 cm^{-1}	1700 cm^{-1}	2920 cm^{-1}	2920 cm^{-1}
1600 cm^{-1}	1575 cm^{-1}	1705 cm^{-1}	1700 cm^{-1}
1575 cm^{-1}	1550 cm^{-1}	1600 cm^{-1}	1600 cm^{-1}
1500 cm^{-1}	1480 cm^{-1}	1570 cm^{-1}	1570 cm^{-1}
1475 cm^{-1}	1420 cm^{-1}	1495 cm^{-1}	1505 cm^{-1}
1260 cm^{-1}	1230 cm^{-1}	1445 cm^{-1}	1445 cm^{-1}
840 cm^{-1}	840 cm^{-1}	1240 cm^{-1}	1240 cm^{-1}
-	-	840 cm^{-1}	840 cm^{-1}

REFERENCES

1. A.C.Griffin and S.J.Havens, J. Polym. Sci. Polym. Phys. Ed., 19, 951 (1981).
2. H.B.Donahoe, E.Louis, V.Benjamin Leon, Fennoy and Greiff, J. Org. Chem., 26, 474 (1961).
3. P.E.Slade Jr. (Ed.), "Techniques and Method of Polymer Evaluation", Vol.4, Marcel Dakker, Inc, New York, p.478 (1975).
4. G.W.Gray, Molecular Structure and the Properties of Liquid Crystals, Academic Press, London, (1962).
5. R.A.Vora and Miss R.S.Gupta, Mol. Cryst. Liq.Cryst., 64(14), 215 (1981).
6. R.A.Vora, Nilesh Dixit, G.D.Karadkar and R.G.Patel, Presented at the IX International Conference on Liquid Crystal, Bangalore, India, Dec. (1982), Accepted for publication in J. Mol. Cryst. Liq. Cryst.,