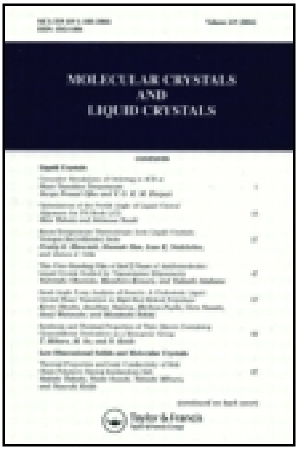

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Polymeric azo Mesogens - II

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POLYMERIC AZO MESOGENS - II

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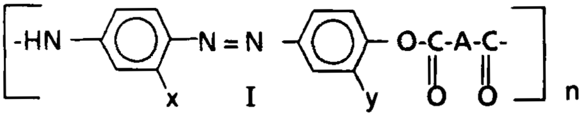
Abstract: In continuation of earlier work, more polyesteramide systems with azo central linkage are synthesized and studied to evaluate the effect of chemical constitution on mesogenic polymers. Polymeric azo mesogens (I) are obtained by condensing substituted 4-amino-4'-hydroxy azobenzenes with different diacid chlorides.



I

Mono and di-substituted azobenzene moieties were incorporated in the polymer system - I. The diacid moiety was changed. The diacid moiety obtained from 1,2-bis (4'-carboxy phenoxy) ethane and 1,4-bis (4'-carboxy phenoxy) butane was conducive to mesomorphism and the polymers exhibited nematic phases. p-Phenylene, m-phenylene and adipoyl moieties were not conducive to mesomorphism. The lateral substituents affect the solid-mesogenic transition temperatures markedly. The polymers were characterized by elemental analysis and IR spectra. Model compounds were prepared to understand the mesogenic behavior of polymers. Visible spectra and TGA studies were carried out for some of the mesogenic polymers.

INTRODUCTION

Recent development in the field of polymers and fibers has shown that liquid crystalline order endows plastic and fibers with extraordinary physical properties. The technological applications and possibility of large structural variations have given impetus to many researchers to synthesize and study mesogenic ploymers. The synthesis and characterization of polymers with amide and ester linkages has become interesting because of their increased thermal stability and thermotropic properties[1-3]. With this in view a number of monomers having amino and hydroxy terminal groups and azo groups as a central linkage were prepared. By using these monomers, different poly azo mesogens with amide and ester linkages were synthesized and reported.[4] In continuation of that, two more monomers substituted at different positions were prepared and were condensed with different diacid chlorides to obtain poly azomesogens with ester and amide linkages.

EXPERIMENTAL

PREPARATION OF DIACIDS

The following diacids were prepared according to the known methods described in the literature.

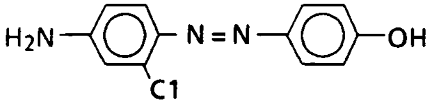
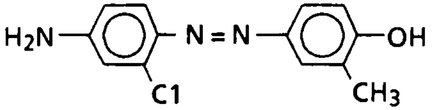
a. 1,2-bis (4'-carboxy phenoxy) ethane[5]

b. 1,4-bis(4'-carboxy phenoxy) butane[5]

c. p-azoxy benzoic acid[6,7]

PREPARATION OF AMINO-HYDROXY-AZOBENZENES

o-Chloro-p-nitroaniline was diazotized and coupled with phenol and o-cresol respectively according to the conventional method.[8] These nitro-hydroxy-azobenzenes were reduced in mild reducing conditions by using solution of sodium sulfide to get the following azobenzene derivatives.[9,10]

Compound	Code	Melting Point °C
	C	170 (Reported 170°C)[10]
	M	171-172

PREPARATION OF POLYMERS

Diacids were refluxed with thionylchloride and pyridine (one or two drops) to obtain diacidchloride. Excess of thionylchloride was distilled-off under vacuum. Solution polycondensation was carried out by reacting respective diacid chloride with amino-hydroxy azobenzene derivatives at 0°-5°C by using pyridine as a solvent. The temperature of reaction mixture was raised to room temperature and stirred for different time intervals as indicated in Tables 1 and 2. The polymeric materials were separated by adding reaction mixture to 1:1 ice-HCl mixture, followed by filtration and purification by solvent (N-methyl-2 pyrrolidone)-non solvent (ethanol) method. Polymeric materials were dried under vacuum.

PREPARATION OF MODEL COMPOUNDS

A method modified by Dave and Vora[11] was used to prepare p-n-decyloxybenzoic acid and p-n-decyloxy benzoic acid chloride was reacted with azobenzene derivatives to obtain mesogenic model compounds containing ester and amide linkages[12].

POST POLYMERIZATION

0.5 gms of the polymers CPEA-1d and CPEAM-1d were heated at 250^0-260^0 C with 0.005 gms of calcium acetate under nitrogen atmosphere and reduced pressure (25 mm of Hg) for 3 hours for the post polymerization. The post polymerized samples, (CPPEA-1d and CPPEM-1d) do not melt up to 300^0 C and their intrinsic viscosities are 0.2538 dl$\bar{g}^1$ and 0.2418 dl$\bar{g}^1$ respectively.

CHARACTERIZATION

The monomers, model compounds and polymers were characterized by elemental analysis and IR spectra.

TRANSITION TEMPERATURE MEASUREMENTS:

A polarizing microscope provided with mettler FP-2 heating stage was used to observe mesomorphism of the polymeric samples. The transition temperatures are recorded in Tables 1-2. The texture of mesophase observed was typical of the nematic mesophase. However, as polymer post-polymerizes, droplet could not be observed on cooling which is one of the characteristic properties of a nematic mesophase. To ascertain nematic mesophase of polymers further, the low molecular weight nematogen, methyl 4-(4'-n-ethoxy bezoyloxy)-benzylidene-4"-aminobenzoate was used for the contact method

$$\left[K \xrightarrow{187^0 C} N \xrightarrow{350^0 C} \text{decomposition} \right]^{13}$$

VISCOSITY MEASUREMENTS

Viscosity of N-methyl-2-pyrrolidone solutions (0.5%) of polymers was measured at 30⁰C by using Ubblehode viscometer. Intrinsic viscosity [η] is calculated by using one point formula[14] and data are recorded in Tables 1 and 2.

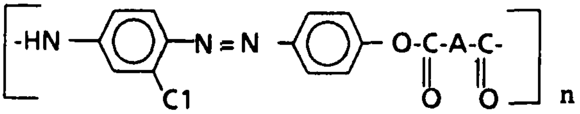
TGA AND VISIBLE SPECTRA

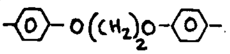
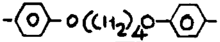
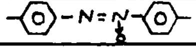
TGA results of representative polymers are recorded in Table 3. The visible spectra of monomers and representative polymers are recorded in Figure 1.

RESULTS AND DISCUSSION

Reference to Tables 1 and 2 shows that polyesteramides of laterally substituted azobenzene moiety and flexible aromatic acid moiety exhibit nematic mesophases. Polymers with p-phenylene, m-phenylene, azoxybenzene and adipoyl moiety of the acids did not exhibit any mesophase. The azobenzene moiety provide rigid moiety, where as aromatic diacid with flexible moiety probably meets the requirement of flexible spacers. However, one would expect polyesteramides with adipoyl moiety to exhibit mesomorphism. It seems that the flexibility of an aliphatic diacid with four methylene spacers is not appropriate for the exhibition of mesomorphism. It would be quite interesting to note that even two lateral substituents on

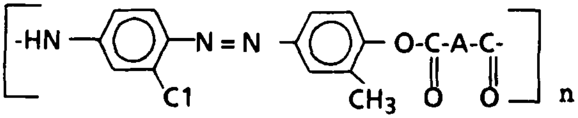
TABLE 1

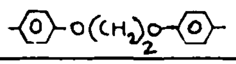
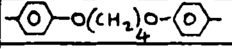
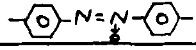


Code	A	Stirr-ing Hrs.	Transition Temp. °C			$[\eta]$ dlg^{-1}
			Smectic	Nematic	Isotropic	
CPEA-1a		1	--	149	267P	0.1670
CPEA-1b	"	2	--	164	269P	0.1741
CPEA-1c	"	3	--	177	261P	0.1798
CPEA-1d	"	5	--	186	262P	0.1798
CPEA-2a		1	--	152	257P	0.1290
CPEA-2b	"	5	--	158	270P	0.1422
CPEA-3		1	--	--	270	0.1422
CPEA-4	$-(CH_2)_4-$	1	--	--	198D	0.1290
CPEA-5		1	--	--	275D	0.1422
CPEA-6		1	--	--	275D	0.1422

P = Further Polymerization D = Decomposition

TABLE 2



Code	A	Stirring Hrs.	Transition Temp. °C			$[\eta]$ dlg^{-1}
			Smectic	Nematic	Isotropic	
CPEAM-1a		1	--	159	286P	0.1553
CPEAM-1b	"	2	--	151	212P	0.1670
CPEAM-1c	"	3	--	168	277P	0.1741
CPEAM-1d	"	5	--	188	270P	0.1741
CPEAM-2a		1	--	141	239P	0.1365
CPEAM-2b	"	5	--	128	260P	0.1422
CPEAM-3		1	--	--	289	0.1610
CPEAM-4	$-(CH_2)_4-$	1	--	--	232D	0.1290
CPEAM-5		1	--	--	290D	0.1422
CPEAM-6		1	--	--	292D	0.1290

P = Further Polymerization D = Decomposition

TABLE 3. Thermo Gravimetric Analysis.

Temperature °C	200	250	300	350	400	450	500	550	600	650	700	750	800
% Weight Loss													
CPEA-1d	1.5	2.6	5.3	10.6	31.6	40.0	49.0	91.0	97.8	--	--	--	--
CPEAM-1d	2.5	5.0	10.0	17.5	35.0	46.0	49.0	51.5	53.5	55.0	57.0	58.5	59.5

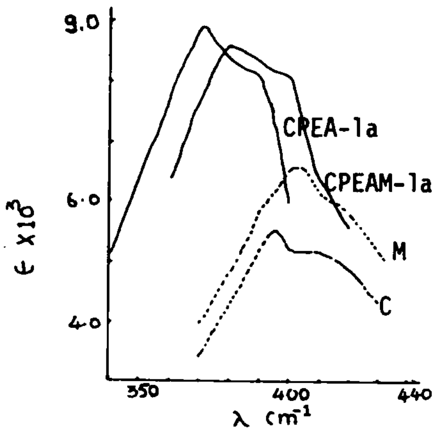


FIGURE 1. Visible Spectra

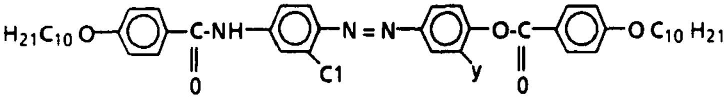
azobenzene moiety does not deter the molecules from exhibition of mesophases. The effect of lateral substitution on solid-mesogenic transition temperatures of polyesteramides is similar to the one observed on low molecular weight liquid crystals. Polymers having lateral chloro and chloro and methyl substituents have lower solid-mesomorphic transition temperatures compared to unsubstituted polymers[4].

Polymeric systems are complex and comparison of mesogenic properties of different polymers would be normally qualitative, if intrinsic viscosity or degree of polymerization of different polymers are not taken into consideration. Reference to Tables 1 and 2 shows that the stirring hours up to a certain limit help to obtain polymers with higher intrinsic viscosity indicating that degree of polymerization is highest for five hours stirring time. As the intrinsic viscosity increases, the solid-mesomorphic transition temperatures also increases. It would be more appropriate to compare nematic-isotropic transition temperatures, however due to post-polymerization effect, polymer solidifies and melting points are raised beyond 300°C.

The increase in flexibility also decreases solid-mesomorphic transition temperatures. Polymers CPEA-2b and CPEAM-2b have lower solid-mesomorphic transition temperatures compared to polymers CPEA-1d and CPEAM-1d (Table 1 and 2).

Thermogravimetric analysis of representative polymeric azomesogens indicated that these poly azomesogens exhibit good thermal stability. They are quite stable up to 300°C (10% weight loss, Table 3). Visible spectra of monomers and polymers indicated the shift of λ_{max} (Figure 1) in the polymer samples.

The model compounds M_1 and M_2 were synthesized to understand the mesogenic behavior of polymers.



Code	Y	Transition Temperatures °C Smectic	 Nematic	 Isotropic
M1	H	122	--	166
M2	CH_3	93	146	159

Model compound having ester and amide central linkages exhibit only smectic phase with only one lateral chloro substituent. Two lateral substitution in the molecule results in a model M_2 which exhibits smectic and nematic phases. Moreover, the reference to mesogenic behavior of both the model compounds indicates that number of substituents also play their role in the exhibition of mesomorphism. None of the polymers exhibit smectic mesophase. One would expect that if model compound exhibits smectic mesophase the polymer may exhibit smectic mesophase. It has been observed that in the polymeric systems many factors play their role. Increase in degree of polymerization is known to eliminate smectic phase, induce nematic phase and in some cases result into a non-mesogenic polymer.[15,16]

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