SYNTHESIS AND CHARACTERIATION OF NOVEL POLY (ESTER AMIDE)s CONTAINING BENZTHIAZOLE HETEROCYCLIC RING

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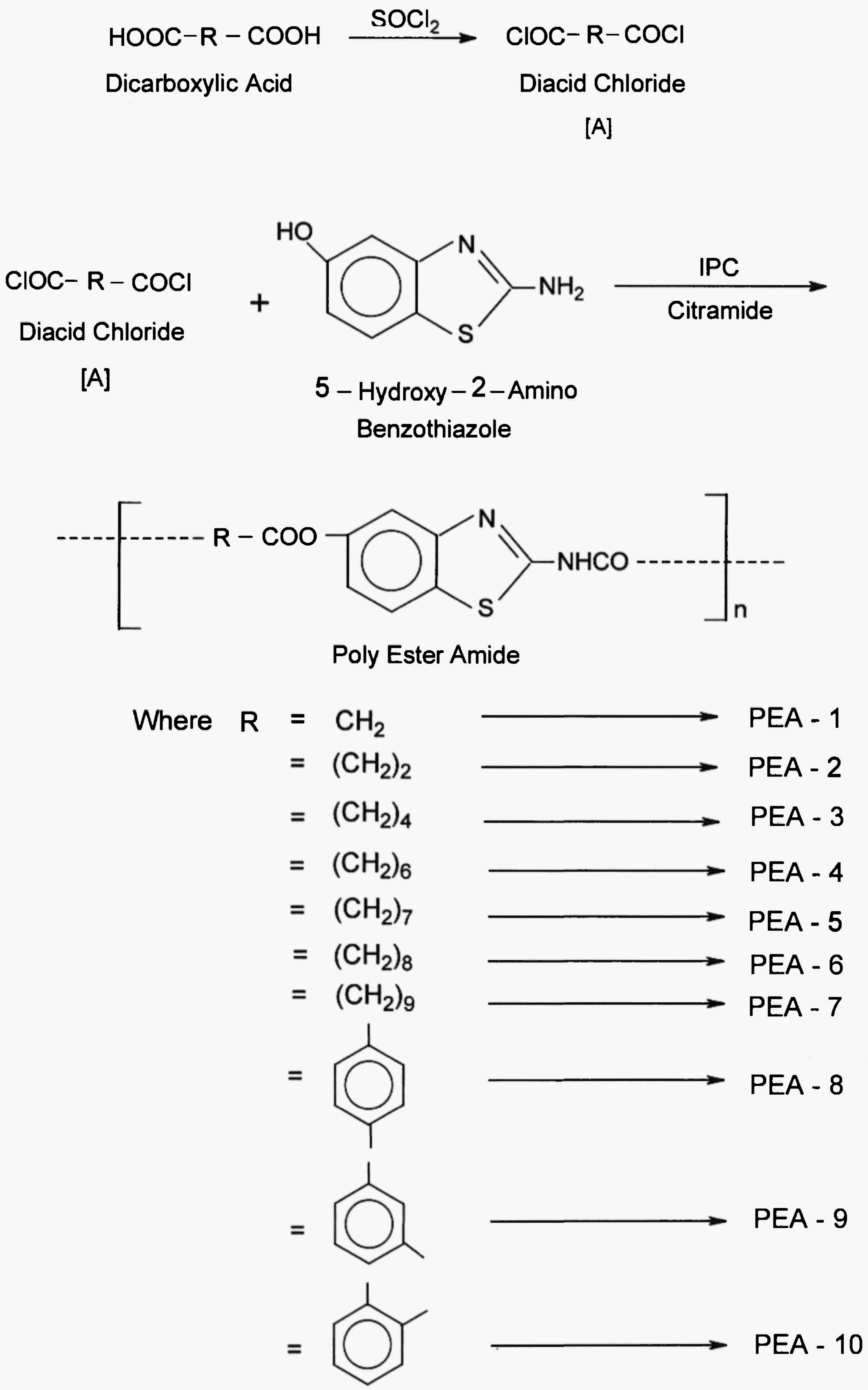
Abstract: The novel Poly (ester-amide)s (PEAs) were prepared by inrter-facial polycondensation of 5 – hydroxy - 2 – amino benzthiazole with various di-basic acid chlorides. The PEAs were characterized by elements analysis, IR spectra studies, $\overline{M}n$ estimated by non aqueous conductometric titration and thermogravimetry.The electric conductivity of all the poly (ester amide)s PEAs was also measured at room temperature and it was found that the PEAs have semiconducting properties.

Keywords: - Polyester, Polyamide, polyester-amide, IR spectral studies, electrical conductivity, Number average molecular weight ($\overline{M}n$).

INTRODUCTION

The polyester and polyamide are individual polymers and marketed industrially. Both have excellent properties for the variety of industrial applications. Both are also known for engineering plastics. The clubbing of both the groups says amide and ester in to one polymer chain has not been developed so far. However, numbers of reports are based on interacting blends of polyester and polyamide or blocked polymer [1-3]. The area of polymerization of aminophenol with di-basic acid, which afford polyester-amide, has been developed from our laboratory [4]. In this context the work presented in this communication is based on studied on poly(ester-amide)s derived from 5 – hydroxy - 2 – amino benzthiazole and dibasic acid chlorides. The whole research is scanned in scheme-1.


HOOC−R − COOH
SOCl2
ClOC− R− COCl
Dicarboxylic Acid
Diacid Chloride
[A]
ClOC− R − COCl
Diacid Chloride
[A]
+
HO
N
S
NH2
IPC
Citramide
5 – Hydroxy – 2 – Amino Benzothiazole
R − COO
NHCO
n
Poly Ester Amide
Where R = CH2 → PEA - 1
= (CH2)2 → PEA - 2
= (CH2)4 → PEA - 3
= (CH2)6 → PEA - 4
= (CH2)7 → PEA - 5
= (CH2)8 → PEA - 6
= (CH2)9 → PEA - 7
= → PEA - 8
= → PEA - 9
= → PEA - 10

Scheme-1

Table-I: Characterization of polyesteramide (PEAs)

PEA Sample	Mole Formula of Repeating Unit	Mol. Wt. of Repeating Unit	Elemental Analysis					
			% C		*% H*		*%N*	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
PEA – 1	$C_{10}H_6O_3N_2S$	234	51.58	50.80	2.56	2.10	11.96	11.50
PEA – 2	$C_{11}H_8O_3N_2S$	248	53.22	52.90	3.22	2.80	11.29	11.00
PEA – 3	$C_{13}H_{12}O_3N_2S$	276	56.52	56.10	4.34	4.10	10.14	9.90
PEA – 4	$C_{15}H_{16}O_3N_2S$	304	59.21	58.80	5.26	5.00	9.21	8.90
PEA – 5	$C_{16}H_{18}O_3N_2S$	318	60.37	60.10	5.66	5.20	8.80	8.50
PEA – 6	$C_{17}H_{20}O_3N_2S$	332	61.44	61.00	6.02	5.80	8.43	8.10
PEA – 7	$C_{18}H_{22}O_3N_2S$	346	62.42	62.10	6.35	6.00	8.09	7.80
PEA – 8	$C_{15}H_8O_3N_2S$	296	60.81	60.40	2.70	2.20	9.45	9.20
PEA – 9	$C_{15}H_8O_3N_2S$	296	60.81	60.30	2.70	2.60	9.45	9.30
PEA – 10	$C_{15}H_8O_3N_2S$	296	60.81	60.50	2.70	2.50	9.45	9.10

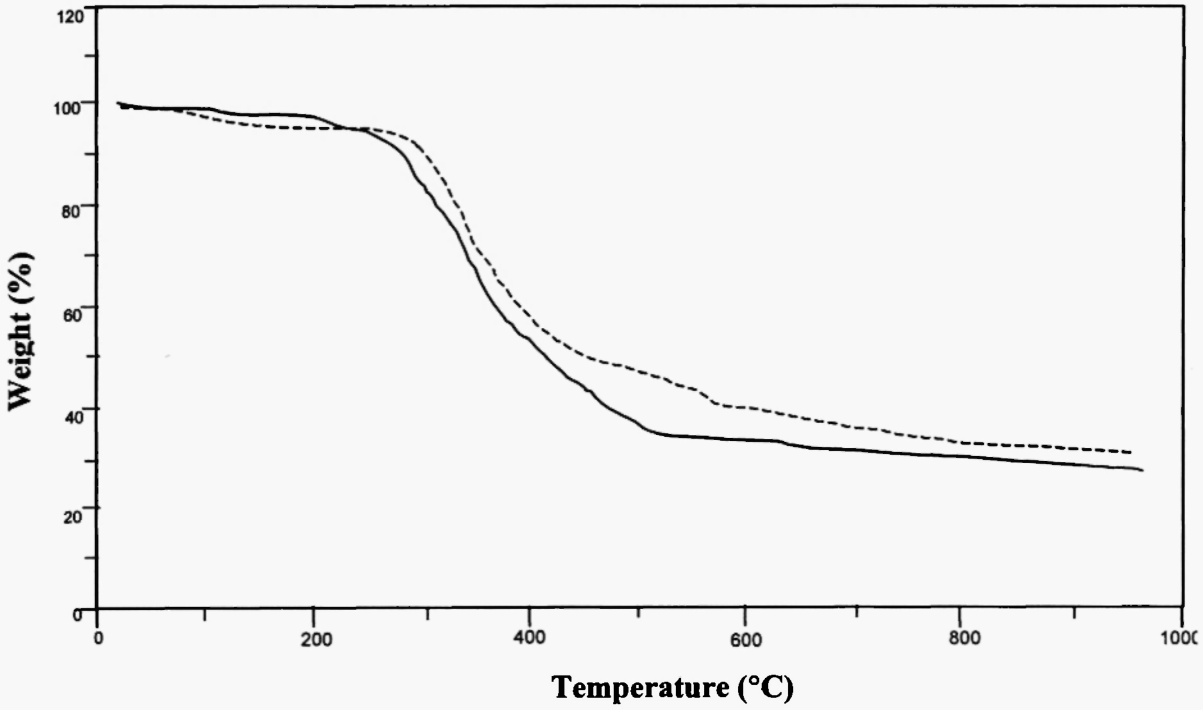
Table-II: Electrical conductivity of PEAs

PEA samples	Electrical conductivity (σ) at 303 °K ($\Omega \cdot cm^{-1}$)
PEA – 1	3.1×10^{-8}
PEA – 2	8.2×10^{-8}
PEA – 3	5.3×10^{-9}
PEA – 4	9.6×10^{-10}
PEA – 5	8.8×10^{-10}
PEA – 6	6.7×10^{-10}
PEA – 7	3.2×10^{-11}
PEA – 8	7.3×10^{-9}
PEA – 9	2.3×10^{-9}
PEA – 10	1.9×10^{-9}

Table-III: Number average molecular weight ($\overline{Mn}$) determination of PEAs and by non-aqueous conductometric titration.

PEA Sample	M mol of tetra–n–butyl ammonium hydroxide at y break (to neut. –COOH group)	$\overline{Mn} = \frac{100}{y \cdot 10^{-3}}$
PEA – 1	48	2083
PEA – 2	57	1754
PEA – 3	46	2174
PEA – 4	44	2273
PEA – 5	40	2500
PEA – 6	30	3333
PEA – 7	29	3448
PEA – 8	34	2941
PEA – 9	30	3333
PEA – 10	33	3030

Figure-I: Thermo gravimetric analysis of poly (urethane-urea)s (PEAs)



EXPERIMENTAL

Materials: All the chemicals used were of analytical grade or laboratory grade.

Procedure

To a well-stirred solution of 5 – hydroxy - 2 – amino benzthiazole in dilute NaOH a solution of dibasic acid chloride in dichloro ethane was added. The resulting mixture was found as an interfacial layered. The interfacial polycondensation was existing by adding of phase transfer catalyst say Citramide. The reaction temperature was maintained at 50 - 60 °C for 2 hours. The polymer was precipitate out in the organic layer, separated and air-dried. Finally, the polymer was treated with diluted alkali to covert remaining chloride into acid.

Measurements

C,H,N contents of polymer samples were estimated by using C,H,N,O and S elemental analyzer, Carlo Erba, Italy. The IR spectra of polymers were scanned in KBr pellets on Perkin Elemer 257 spectrophotometer, Number average molecular weights $(\overline{Mn})$ of polymers were estimated by non-aqueous conductometric titration [3]. It was carried out respectively in pyridine (for –COOH end group) against standard tetra–n–butylammonium hydroxide in pyridine as a titrate. Digital conductometre, Toshniwal, India was used for this purpose. The values of molecular weight $(\overline{Mn})$ of all polymer samples were calculated following the method reported by one of the author [HSP] [7]. Thermo gravimetric analyses for polymers were carried out on Du Pont thermo balance in air at a heating rate of 10 °K min^{-1}. The electrical conductivity of each of PUU sample was measured on pellets (1cm diameter, 0.45cm thickness) at room temperature (30±1 °C) using a Million Megohmmeter RM 160 MK IIA BPL, India. The preparations of the pellets of all the PEAs samples and other details have been described in an earlier communication [4].

Results and Discussion

The poly (ester – amide)s (PEAs) formation is performed by condensation reaction of -COCl group with NH_2 and OH groups. The PEAs shown in reaction scheme are furnished in Table I. They were white or dark brown solid powders. They did not melt up to 250 °C and are insoluble in common organic solvents. Elemental contents (C, H, N) (Tab. I) of the polymers are consistent with the predicted structure (reaction scheme).

IR spectra (not shown) of all the PEAs are identical in almost all the aspects. They comprise important IR spectral features of ester and amide linkages. The IR bends between 1730 - 1715 cm^{-1}, 1700-1670 cm^{-1} and 1580 - 1520 cm^{-1} may be due to ester and amide linkages [3]. The other IR spectra feature are due to aromatic and aliphatic moieties present in monomers.

As the produced polymers are insoluble in organic solvents, the colligative properties (i.e. viscosity, osmometry) have not been studied. Hence two number average molecular weight ($\overline{M}n$) of all the polymer samples has been measured by end group (-COOH) by non-aqueous conductometric titration. The result of Mn values are furnished in Table-III. Typical TG thermograms of PEAs are shown in figure – 1. Inspection of the TG thermograms is reveals that all the PEA decompose in one step. They start their degradation about 225 °C, losses their wt. rapidly in between 300 to 600 °C. The electrical conductivity measured at room temperature of all PEAs samples are shown in Table-II and they are in the range of 3.1×10^{-8} to 3.2×10^{-11} Ωcm^{-1} depending upon the nature of polymer. The examination of the results reveals that the produced PEAs can be ranked as semiconductors. The produced PEAs are insoluble and hence they cannot be processed. This is in progress. The application of PEAs is under progress.

Conclusion

In conclusion, the produced polyester-amides have amorphous nature. Having both groups, the formation of PEAs is feasible. Due to electron containing group, they have semiconducting properties. The fabrication of such polymers by modification into structure is under progress.

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