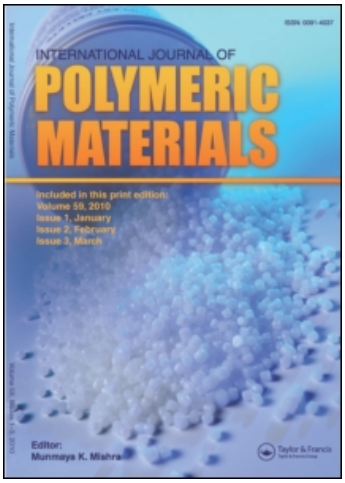

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Poly (Urethane-Urea)s: Part-4

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Poly(Urethane-Urea)s: Part-4

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Poly(urethane-urea)s (PUUs) were prepared by polycondensation of different amino-alcohols and aminophenols/naphthols with various diisocyanates. The resultant poly(urethane-urea)s were characterized by elemental analyses, IR spectral studies, number average molecular weight ($\overline{Mn}$) estimated by non-aqueous conductometric titration and thermogravimetry. The electrical properties of these polymers have also been measured at room temperature.

Keywords: Poly(urethane-urea)s; diisocyanates; aminoalcohol; aminophenols/naphthols; molecular weight; electrical properties

1. INTRODUCTION

Each of polyureas and polyurethanes are well known candidates for industrial polymer applications [1]. The introduction of both the group viz. urea and urethane into one polymer chain has received no more attention yet. However only few poly(urethane-urea)s are reported from aminoglucose [2] or from mixture of diol, diamine and diisocyanate [3,4]. As it might give polymers having important properties, the present authors adopted such type of polymer research by condensation of monomer 4-aminophenol having both amino and hydroxy groups [5]. In continuation of this work [5], the present paper comprises the synthesis and characterization of novel poly(urethane-urea)s from i) aminoalcohol synthetic route presented

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in Schemes 1 and from aminophenol naphthol synthetic route presented in Scheme 2.

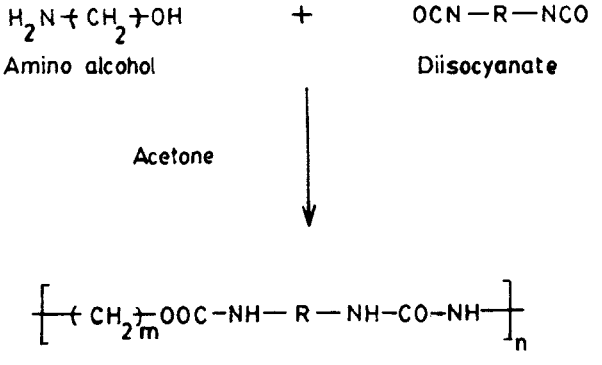
2. EXPERIMENTAL

2.1. Materials

All the chemicals used were of analytical grade of laboratory grade.

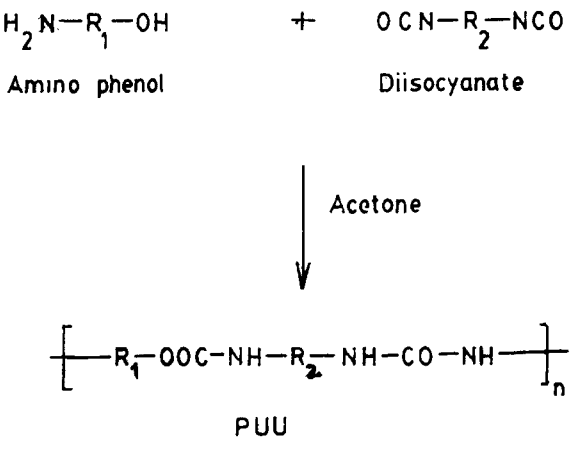
2.2. Synthesis of Poly(urethane-urea)s

To an ice cooled solution of aminoalcohol listed in Scheme 1 (0.01 mole) or aminophenol listed in Scheme 2 in dry acetone (50 ml) a solution of diisocyanate in 50 ml dry acetone was added gradually with constant stirring. The stirring was continued at room temperature for 1 hour. Then it was refluxed for 2 hours on a water bath. The resulting solid product was then filtered off and air-dried (95% yield).



Where, m = a : 2 R = 1 : Toluene
b : 3 2 : Hexamethylene
c : 4 3 : 4,4'-Methane diphenylene
4 : Isophorone

SCHEME 1



R_1 = a : 3-methyl-1,4-phenylene
b : 2-methyl-1,4-phenylene
c : 3,5-dichloro-1,4-phenylene
d : 1,7-naphthalele
e : 2-benzylene

R_2 = 1 : Toluenyl
2 : hexa methylene
3 : 4,4' methane diphenylene
4 : isophorylene

SCHEME 2

2.3. Measurements

C, H, N contents of all polymers were estimated using C, H, N, O and S elemental analyser, Carlo Erba, Italy. The IR spectra of polymers were scanned in KBr pellets on Perkin Elmer 257 spectrophotometer, Number average molecular weights ($\overline{Mn}$) of polymers were estimated by non-aqueous conductometric titration. It was carried out respectively in formic acid (for $-NH_2$ end group) against standard perchloric acid and in pyridine (for — OH end group) against standard

sodium methanolate. Digital conductometer, Toshniwal, India was used for this purpose. The value of molecular weight($\overline{Mn}$) of all polymer samples were calculated following the method reported by reported method [6]. Thermogravimetric analysis for polymers were carried out on Du Pont thermobalance in air at a heating rate of 10 K min^{-1}. The electrical conductivity of each of PUUs samples was measured on pellets (1 cm diameter, 0.45 cm thickness) at room temperature ($\sim 30 \pm 1$°C) using a Million Megohmmeter RM160 MK IIA BPL, India. The preparation of the pellets of all the PUUs samples and other details have been adopted from literature [7].

3. RESULTS AND DISCUSSION

The poly(urethane-urea) (PUU) formation is performed by facile reaction of NH_2 and OH groups with —NCO group. The PUUs shown in reaction scheme are furnished in Tables I and II. They are dark brown solid powders. They do not melt up to 250°C and are insoluble in common organic solvents. Elemental contents (C, H, N) (Tabs. I and II) of the polymers are consistent with the predicted structure (reaction scheme).

IR spectra (not shown) of all the PUUs are identical in nature. They comprise important IR spectral features of urea and urethane linkages.

TABLE I Characterization of poly(urethan-urea)s (PUUs) based on aminoalcohols

PUU Sample	*Mole formula of repeat unit*	*Mol. wt. of repeat unit*	*ELEMENTAL ANALYSIS*						$\overline{Mn}$*	*Elect. Conductivity (σ) at 303 K (Ω cm)*
			% C		*% H*		*% N*			
			calcd.	*found*	*calcd.*	*found*	*calcd.*	*found*		
1a	$C_{11}H_{13}N_3O_3$	235	56.17	55.9	5.53	5.4	17.87	17.7	1650	6.4×10^{-10}
1b	$C_{12}H_{15}N_3O_3$	249	57.83	57.5	6.02	5.9	16.87	16.8	1800	7.1×10^{-12}
1c	$C_{13}H_{17}N_3O_3$	263	59.32	58.8	6.46	6.3	15.79	15.6	1900	8.9×10^{-9}
2a	$C_{10}H_{19}N_3O_3$	229	52.4	52.1	8.3	8.1	18.34	18.2	2500	8.1×10^{-10}
2b	$C_{11}H_{21}N_3O_3$	243	54.32	53.9	8.64	8.5	17.29	17.1	2700	6.9×10^{-12}
2c	$C_{12}H_{23}N_3O_3$	257	56.03	55.7	8.95	8.8	16.34	16.2	2850	7.3×10^{-9}
3a	$C_{17}H_{17}N_3O_3$	311	65.59	66.3	5.47	5.3	13.5	13.2	1800	6.6×10^{-10}
3b	$C_{18}H_{19}N_3O_3$	325	66.46	66.1	5.85	5.7	12.92	12.7	2000	7.4×10^{-12}
3c	$C_{19}H_{21}N_3O_3$	339	67.26	66.9	6.19	6.1	12.39	12.2	2050	8.4×10^{-9}
4a	$C_{14}H_{25}N_3O_3$	283	59.36	59.0	8.84	8.6	14.84	14.6	2800	8.9×10^{-10}
4b	$C_{15}H_{27}N_3O_3$	297	60.61	60.4	9.09	8.9	14.14	14.0	3000	7.8×10^{-12}
4c	$C_{16}H_{29}N_3O_3$	311	61.74	61.6	9.33	9.1	13.5	13.3	3150	9.4×10^{-9}

* Estimated by non-aqueous conductometric titration.

TABLE II Characterization of poly(urethan-urea)s (PUUs) based on aminophenols

PUU Sample	*Mole formula of repeat unit*	*Mol. wt. of repeat unit*	*ELEMENTAL ANALYSIS* % C		% H		% N		$\overline{Mn}$*	*Elect. Conductivity (σ) at 303 K (Ω cm)*
			calcd.	*found*	*calcd.*	*found*	*calcd.*	*found*		
1a	$C_{16}H_{15}N_3O_3$	297	64.65	64.3	5.05	4.8	14.14	14.0	1850	6.81×10^{-10}
1b	$C_{15}H_{21}N_3O_3$	291	61.86	61.5	7.22	7.1	14.43	14.1	2950	7.9×10^{-11}
1c	$C_{22}H_{19}N_3O_3$	373	70.78	70.6	5.09	4.8	11.26	11.0	3050	8.9×10^{-9}
1d	$C_{19}H_{27}N_3O_3$	345	66.09	66.0	7.83	7.6	12.17	11.9	3500	4.6×10^{-12}
2a	$C_{16}H_{15}N_3O_3$	297	64.65	64.3	5.05	4.8	14.14	14.0	1900	3.6×10^{-10}
2b	$C_{15}H_{21}N_3O_3$	291	61.86	61.6	7.22	6.9	14.43	14.1	3000	7.4×10^{-11}
2c	$C_{22}H_{19}N_3O_3$	373	70.78	70.3	5.09	4.9	11.26	11.0	3100	9.1×10^{-9}
2d	$C_{19}H_{27}N_3O_3$	345	66.09	65.8	7.83	7.7	12.17	12.0	3550	6.2×10^{-12}
3a	$C_{15}H_{11}N_3O_3Cl_2$	352	51.14	50.9	3.13	3.0	11.93	11.8	2200	6.1×10^{-10}
3b	$C_{14}H_{17}N_3O_3Cl_2$	346	48.55	48.3	4.91	4.7	12.14	12.0	3650	7.9×10^{-11}
3c	$C_{21}H_{15}N_3O_3Cl_2$	428	58.89	58.6	3.5	3.3	9.81	9.6	3450	8.3×10^{-9}
3d	$C_{18}H_{23}N_3O_3Cl_2$	400	54.00	53.7	5.75	5.5	10.5	10.1	4100	4.1×10^{-12}
4a	$C_{19}H_{15}N_3O_3$	333	68.47	68.2	4.5	4.2	12.62	12.4	2100	8.1×10^{-10}
4b	$C_{18}H_{21}N_3O_3$	327	66.05	65.7	6.42	6.0	12.84	12.7	3350	7.2×10^{-11}
4c	$C_{25}H_{19}N_3O_3$	409	73.35	73.0	4.65	4.4	10.27	10.0	3400	8.3×10^{-9}
4d	$C_{22}H_{27}N_3O_3$	381	69.29	69.1	7.09	6.7	11.02	10.8	3850	4.1×10^{-12}
5a	$C_{16}H_{15}N_3O_3$	297	64.65	64.3	5.05	4.8	14.14	13.8	1800	6.2×10^{-10}
5b	$C_{15}H_{21}N_3O_3$	291	61.86	61.7	7.22	7.0	14.43	13.9	2900	6.6×10^{-11}
5c	$C_{22}H_{19}N_3O_3$	373	70.78	70.6	5.09	4.9	11.26	11.0	3150	7.4×10^{-9}
5d	$C_{19}H_{27}N_3O_3$	345	66.09	65.9	7.83	7.4	12.17	11.9	3600	4.4×10^{-12}

* Estimated by non-aqueous conductometric titration.

The IR bends at 1700 cm^{-1}, 1270 cm^{-1} may be due to urethane linkage and the bands at 1640 cm^{-1}, 1255 cm^{-1} may be due to urea linkage [2]. The other IR spectral features are due to aromatic and aliphatic moieties present in monomers.

The end group analysis of all the polymers give the number average molecular ($\overline{Mn}$) weight (Tabs. I and II). As the produced polymers are insoluble in organic solvents, the colligative properties (i. e. viscosity, osmometry) have not been studied. The thermogravimetric analysis of all the PUUs reveals that they decompose into two stage. The first stage starts from 200°C and the second stage starts from 380°C. The degradation starts at 200°C is indication of urethane groups. It is reported that polyurethanes start their degradation [8]. This might be due to depolymerization i. e. degradation. The urethane linkage convert into isocyanate on the loss at about 200°C. On the basis of the structure of the polymer sample the possible %age wt loss due to this depolymerization during the 1st step of degradation is calculated. The values for the first step in the degradation of the polymer sample are furnished in Tables III and IV. These results confirmed the view that the first step in the degradation of the polymer samples is due to depolymerization of all the 'urethane units' of the polymer chains. The electrical conductivity measured at room temperature of all four PUU samples are shown in Tables I and II and they are in the range of 4.1×10^{-12} to 9.4×10^{-9} $\Omega \cdot cm^{-1}$ depending upon the nature of the

TABLE III Thermogravimetric analysis of poly(urethan-urea)s (PUUs) based on aminoalcohols

PPU SAMPLE	*% AGE WEIGHT LOSS AT TEMP °C*						*LOSS AT 1st STEP (200–300 °C)*	
	200	*300*	*400*	*500*	*600*	*700*	*Calcd.*	*Found*
1a	7.0	19.0	45.0	60.0	80.0	92.0	18.70	18.20
1b	6.0	18.0	42.0	57.0	75.0	92.0	17.70	17.00
1c	4.0	16.0	40.0	52.0	75.0	90.0	16.70	17.30
2a	8.0	20.0	47.0	60.0	80.0	92.0	19.20	19.80
2b	6.0	18.0	43.0	56.0	75.0	92.0	18.10	19.00
2c	4.0	17.0	42.0	56.0	75.0	90.0	17.10	16.80
3a	4.0	15.0	38.0	55.0	75.0	92.0	14.20	14.70
3b	3.0	14.0	36.0	52.0	75.0	92.0	13.50	14.00
3c	3.0	14.0	36.0	52.0	75.0	90.0	13.00	13.50
4a	6.0	17.0	40.0	56.0	80.0	92.0	15.60	15.90
4b	3.0	15.0	38.0	54.0	75.0	90.0	14.80	14.50
4c	3.0	14.0	36.0	53.0	75.0	92.0	14.20	14.80

TABLE IV Thermogravimetric analysis of poly(urethan-urea)s (PUUs) based on aminophenols

PPU SAMPLE	% AGE WEIGHT LOSS AT TEMP °C						LOSS AT 1st STEP (200–300 °C)	
	200	300	400	500	600	700	Calcd.	Found
1a	4.0	15.0	36.0	52.0	75.0	92.0	14.80	14.30
1b	4.0	16.0	42.0	58.0	80.0	92.0	15.10	15.80
1c	2.0	13.0	37.0	50.0	72.0	90.0	11.80	12.30
1d	2.0	12.0	42.0	56.0	75.0	92.0	12.80	13.20
2a	5.0	16.0	38.0	54.0	75.0	92.0	14.80	15.00
2b	4.0	14.0	36.0	52.0	73.0	90.0	15.10	14.90
2c	2.0	13.0	37.0	53.0	75.0	92.0	11.80	12.50
2d	2.0	13.0	38.0	56.0	76.0	92.0	12.80	13.30
3a	4.0	15.0	38.0	53.0	75.0	92.0	12.50	13.00
3b	3.0	13.0	37.0	52.0	75.0	92.0	12.70	12.40
3c	2.0	11.0	35.0	50.0	72.0	90.0	10.30	10.70
3d	2.0	12.0	37.0	52.0	75.0	92.0	11.00	11.50
4a	3.0	13.0	38.0	54.0	75.0	92.0	13.20	14.00
4b	3.0	14.0	36.0	54.0	75.0	92.0	13.50	13.90
4c	2.0	12.0	37.0	54.0	76.0	92.0	10.80	11.30
4d	2.0	12.0	37.0	53.0	73.0	90.0	11.50	12.00
5a	6.0	16.0	40.0	57.0	80.0	92.0	14.80	14.50
5b	4.0	15.0	38.0	54.0	75.0	92.0	15.10	15.70
5c	2.0	11.0	35.0	50.0	72.0	90.0	11.80	12.30
5d	2.0	13.0	37.0	52.0	75.0	92.0	12.80	13.10

polymer. The examination of the results reveals that the produced PUUs can be ranked as semiconductors. The produced PUUs are insoluble and hence they cannot be processed. Hence its modifications in terms of application view the novel PUUs synthesis has been adopted. This is in progress.

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