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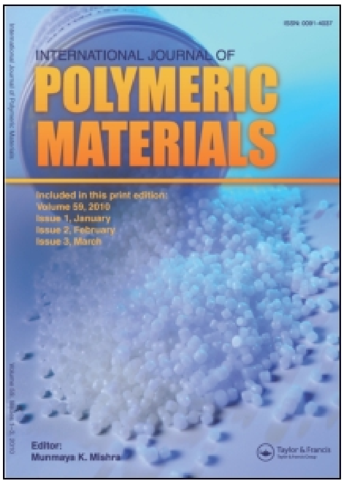

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Synthesis and Characterization of Colored Poly(Urethane-Urea)

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Synthesis and Characterization of Colored Poly(Urethane-Urea)

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Various Poly(urethane-urea)s (PUU)s were prepared by polycondensation of various azo dyes having both amino and hydroxyl group with Toluene 2, 4-diisocyanate. The resultant poly(urethane-urea)s were characterized by the elementary analysis, IR spectral, nonaqueous conductometric titration, and thermogravimetry. The electrical conductivity of these oligomers has also been measured at room temperature.

Keywords: poly(urethane-urea)s, diisocyanates, number average molecular weight, IR spectral studies, electrical properties

INTRODUCTION

Each of polyureas and polyurethanes are well-known candidates for industrial polymers applications [1]. The introduction of both groups, that is, urea and urethane into one polymer chain has received only a little attention as of yet. However, a few poly(urethane-urea)s are reported from amino glucose [2] or from mixture of diol diamine

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and diisocyanate [3]. As it might give polymers having important properties, such a type of polymer research has been pursued by the condensation of monomers having both amino and hydroxy groups (e.g., 4-aminophenol and diisocyanate). The initial work in this direction has been carried out in the authors' laboratory, [4]. In continuation of this work the present article discusses the synthesis and characterization of colored poly(urethane-urea)s. The work is described in Scheme 1.

EXPERIMENTAL

Materials

All the chemicals used were of analytical or laboratory grades.

Synthesis of Azo Disperse Dyes

The azo disperse dyes having structures shown in Scheme 1 where prepared in the same manner. The general process is as follows.

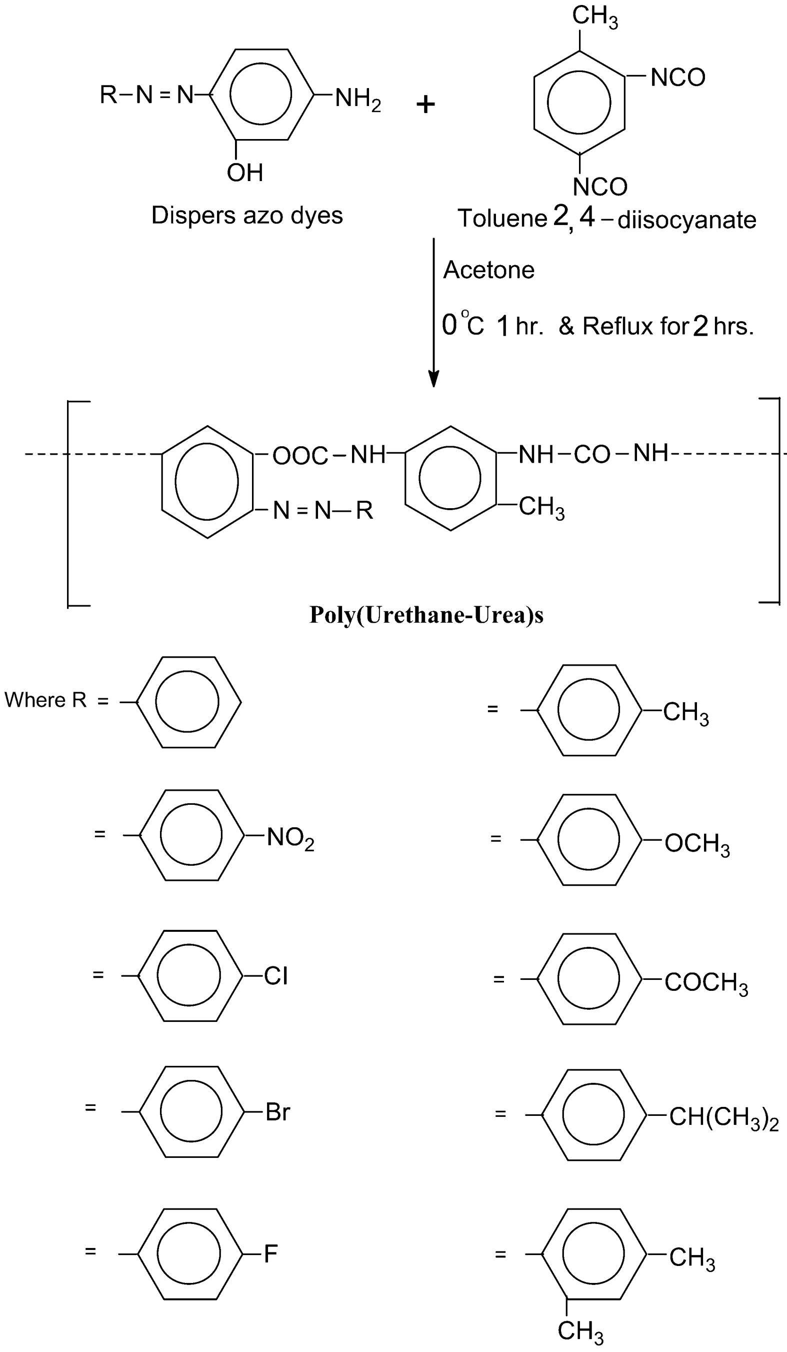
Primary Amine (0.01 mole) was suspended in water (36 ml). Hydrochloric acid (1.08 g, 0.03 mole) was added dropwise to this well-stirred suspension. A solution of sodium nitrite (0.7 gm, 0.01 mole) in water (3 ml), previously cooled to 0°C, was then added. The reaction mass was stirred until a positive test for nitrous acid on starch iodide paper was reached. Excess of nitrous acid was neutralized by adding the required amount of Sulphamic acid. The resulting diazo solution was used for the subsequent coupling reaction.

m-Aminophenol (0.01 mole) was dissolved in solution of Sodium Hydroxide (10%) and the solution was cooled to 0–5°C in an ice bath. To this well stirred solution, the aforementioned diazo solution was then gradually added over an hour at 0–5°C. Then the reaction mixture was stirred for three hours at 0–5°C, maintaining the pH 8.0 by a controlled addition of sodium carbonate solution (10% w/v). The obtained precipitate was filtered and wash with hot H_2O. The yield was around 75%.

Synthesis of Colored Poly(Urethane-Urea)s

All the poly(urethane-urea)s based on azo disperse dyes where prepared in the same manner. The general process is as follows.

To an ice-cooled solution of azo disperse dye sample containing $-OH$ and $-NH_2$ groups (0.01 moles) in dry acetone (50 ml) a solution of Toluene 2,4-diisocyanate (0.01 mole) in 50 ml dry acetone was added


R–N = N–
NH2
OH
+
CH3
NCO
NCO
Dispers azo dyes
Toluene 2, 4 – diisocyanate
Acetone
0 °C 1 hr. & Reflux for 2 hrs.
OOC – NH
N = N – R
NH – CO – NH
CH3
n
Poly(Urethane-Urea)s
Where R =
CH3
NO2
OCH3
Cl
COCH3
Br
CH(CH3)2
F
CH3
CH3

SCHEME 1

gradually with constant stirring. The stirring was continued at room temperature for 1 h. Then it was refluxed for 2 h on a water bath. The resulting solid product was then filtered off and air-dried (95% yields).

MEASUREMENTS

C, H, N contents of the oligomers were estimated using a Carlo Erba, Italy, C, H, N, O and S elemental analyzer. The IR spectra of oligomers were scanned in KBr pellets on Perkin Elemer 257 spectrophotometer, Number average molecular weights ($\overline{\mathrm{M}}$n) of the oligomers were estimated by non-aqueous conductometric titration. It was carried out, respectively, in formic acid (for $-NH_2$ end group) against perchloric acid and in pyridine (for $-OH$ group) against standard sodium methanolate. Digital conductometre, Toshniwal, India, was used for this purpose. The values of number average molecular weight ($\overline{\mathrm{M}}$n) of all oligomers samples were calculated following the method reported by one of the present author [HSP] [5]. Thermo gravimetric analyses for oligomers 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 (1 cm diameter, 0.45 cm thickness) at room temperature (30 ± 1°C) using a Million Me ohmmeter RM 160 MK IIA BPL, India. The preparations of the pellets of all the PUU samples and other details have been described in an earlier communication [6].

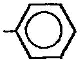
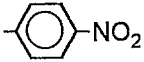
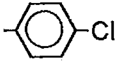
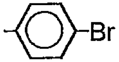
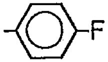
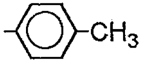
RESULTS AND DISCUSSION

The poly(urethane-urea) (PUU) formation is performed by facile reaction of NH_2 and OH with $-NCO$ groups. The PUUs shown in the reaction scheme are characterized in Table 1. They are solid powders of various colors. They do not melt up to 250°C and are insoluble in common organic solvents. Elemental contents (C, H, N) (Table 1) of the oligomers are consistent with the predicted structures (reaction scheme).

IR spectra (not shown) of all the PUUs are identical in nature. They comprise the important IR spectral features of urea and urethane linkages. The IR bands at 1700 cm^{-1} and 1270 cm^{-1} are due to urethane linkage and the bands at 1640 cm^{-1} and 1255 cm^{-1} are due to urea linkage [7]. The other IR spectral features are due to aromatic and aliphatic moieties present in the monomers.

As the produced oligomers are insoluble in common organic solvents, the colligative properties (i.e., viscosity, osmometry) have not been studied. Therefore, the number average molecular weight ($\overline{\mathrm{M}}$n) of the

TABLE 1 Characterization of Poly(Urethane-Urea)s (PUUs)

PUU sample	R =	Color of sample	Mole formula of repeating unit	Mol. wt. of repeating unit	$\overline{M}n$	Elemental analysis					
						% C		% H		% N	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
PUU-1		Yellow	$C_{21}H_{17}O_3N_5$	387	3450	65.11	65.00	4.39	4.10	18.08	17.80
PUU-2		Dark brown	$C_{21}H_{16}O_5N_6$	432	3030	58.33	58.10	3.70	3.50	19.44	19.10
PUU-3		Brown	$C_{21}H_{16}O_3N_5Cl$	421	3330	59.85	59.50	3.80	3.60	16.62	16.30
PUU-4		Brown black	$C_{21}H_{16}O_3N_5Br$	466	3700	54.07	54.00	3.43	3.30	15.02	14.80
PUU-5		Brown	$C_{21}H_{16}O_3N_5F$	405	3330	62.22	62.00	3.95	3.50	17.28	17.00
PUU-6		Dark brown	$C_{22}H_{19}O_3N_5$	400	4000	66.00	61.90	4.75	4.50	17.50	17.20

(*Continued*)

TABLE 1 Continued

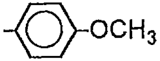
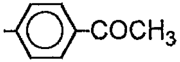
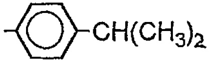
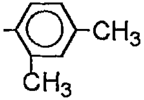
PUU sample	R =	Color of sample	Mole formula of repeating unit	Mol. wt. of repeating unit	$\overline{M}n$	Elemental analysis					
						% C		% H		% N	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
PUU-7		Yellow brown	$C_{22}H_{19}O_4N_5$	417	4340	63.30	63.10	4.55	4.20	17.78	16.30
PUU-8		Brown	$C_{23}H_{19}O_4N_5$	429	4540	64.33	64.20	4.42	4.10	16.31	16.10
PUU-9		Orange	$C_{24}H_{23}O_3N_5$	429	4760	67.13	67.00	5.36	5.10	16.31	16.20
PUU-10		Red	$C_{23}H_{22}O_3N_5$	416	4340	66.34	66.10	5.28	5.00	16.82	16.50

TABLE 2 Electrical Conductivity of PUUs

PUU samples	Electrical conductivity (σ) at 303°K ($\Omega \cdot \mathrm{cm}^{-1}$)
PUU-1	9.1×10^{-8}
PUU-2	2.3×10^{-10}
PUU-3	4.6×10^{-9}
PUU-4	8.3×10^{-9}
PUU-5	7.2×10^{-9}
PUU-6	6.2×10^{-7}
PUU-7	6.9×10^{-7}
PUU-8	7.1×10^{-7}
PUU-9	1.3×10^{-7}
PUU-10	3.2×10^{-7}

oligomer samples has been measured by end group ($-NH_2$ or $-OH$) nonaqueous conductometric titration. The results of $\overline{M}n$ values are furnished in Table 1.

TG thermograms (not shown) of all the PUUs are identical in nature. The thermogravimetry analysis of all the PUUs reveals that they decompose into two stages. The first stage starts from 200°C and the second stage starts from 380°C. The degradation that starts at 200°C may be an indication of the presence of urethane groups in the authors' oligomeric products [8–9]. At this temperature, the urethane linkage converts into an amide linkage with a commensurate weight loss. These results do not confirm the alternative view that the first step in the degradation of the samples is due to depolymerization of the "urethane units" of the oligomers chains.

The electrical conductivities measured at room temperature, of all the PUUs samples are shown in Table 2. They fall in the range of 2.3×10^{-10} to 1.3×10^{-7} Ω cm^{-1} depending on the nature of the oligomers. An examination of the results reveals that the produced PUUs can be ranked as poor insulators. The application of the PUUs is under progress.

CONCLUSIONS

The present work describes the preparation and some properties of colored poly(urethane-urea) oligomers. They are all amorphous colored powders. They have low thermal stability. Having urea and urethane groups, they can be compatible with thermoplastic resins and can be easily used to form colored articles even when processed at high temperatures. Importantly, the colored poly(urethane-urea)s cannot bloom or bleed from the thermoplastic-resin-based articles.

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