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Polyureas: Synthesis and Characterization

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Abstract: Various 4-Arylazo-1, 3-benzenediamine (AABs) derivatives have been synthesized and polycondensed with hexamethylene diisocyanate (HMDI). The resultant poly (4-arylazo-1, 3-benzeneurea-hexamethylene)s (PABUs) have been characterized by elemental analysis, IR spectroscopy and number average molecular weight ($\overline{Mn}$) (Estimated by non-aqueous conductometric titration). Thermal properties of PABUs have been examined by thermogravimetric analysis.

Keywords: Polyureas, Infrared Spectra (IR), Thermogravimetry analysis (TGA), Number average molecular weight ($\overline{Mn}$).

Introduction

Polyureas may be classified as heterochain macromolecules, which contain urea groups in their chain. Although the chemistry and technology of polyureas are of recent origin, the chemistry of ureas dates back over 100 years. Linear polyureas are thermoplastic polycondensation products with aliphatic or aromatic structures. Polyureas or copolyureas containing aliphatic structures exhibit a difference of 50-100°C between melting points and the beginning of decomposition; they are used for castings. Polyureas containing aromatic structures melt near their decomposition temperatures. They are soluble in some organic solvents and can be used for preparation of lacquers, varnishes and coatings [1]. Polyureas were first prepared on a commercial scale at I.G. Farben, employing the reaction between diisocyanate and diamines. Today, polyureas and copolyureas (especially polyurethane polyureas) have many practical applications as foams, elastomers, adhesives, fibers, etc [2-3].

Polymeric colorants offer the advantage of allowing tunability in a range of physical properties such as solubility, absorption, migration, and viscosity. They do not sublime, are non-abrasive, and generally have low toxicity. The range of possible product offered by the joining of the fields of polymer chemistry and color chemistry is virtually inexhaustible. Thus the present article comprises synthesis and characterization, and dyeing performance on nylon and polyester of polyureas.

Experimental

Materials

All the chemicals used were of analytical grade. Various 2-aminobenzothiazoles have been prepared by the methods reported in the literature [4].

Characterization Methods

The C, H, N, S contents have been estimated by Thermofinigen-1101 Flash elemental analyzer (Italy). The sulfur content has been determined by Carius method [5]. IR spectra of all the polymers have been scanned in KBr pellets on a Perkin Elemer 257

spectrophotometer. Number average molecular weights ($\overline{Mn}$) of PUs have been estimated by non-aqueous conductometric titration. The titration has been carried out in formic acid against perchloric acid as titrant. A digital conductometer, Toshniwal, India was used for this purpose. Values of the number average molecular weight ($\overline{Mn}$) of all polymer samples have been calculated by the method reported in literature [6]. Thermogravimetric analysis for polymers was carried out on Du Pont thermobalance in air at a heating rate of 10°K min^{-1}.

Procedures

Synthesis of Azo Disperse Dyes

To 5.5 mmol m-phenylene diamine were added 1 ml concentrated hydrochloric acid and 10 ml water to make its salt solution. 5.5 mmol 2-aminobenzothiazoles, 10 ml H_2O and 5.5 mmol $NaNO_2$, were mixed to form a paste, which was poured into a mixture of crushed ice and 1.5 ml concentrated hydrochloric acid. The reaction was carried out for 0.5 h in an ice bath. The diazonium salt solution was added slowly into the solution of m-phenylenediamine salt during stirring and the mixture reacted for 1 h. After neutralizing with ammonia water, the product was filtered and washed with water until neutral [7].

Synthesis of Colored Polyureas (PUs)

All the polyureas based on azo disperse dyes AAB, were prepared in a similar manner. The general process is as follows:

To an ice cooled solution of azo disperse dye sample (0.01 moles) in dry tetrahydrofuran (50 ml) a solution of hexamethylene diisocyanate (0.01 mole) in 50 ml dry tetrahydrofuran was added gradually with constant stirring. The colloidal suspension which formed immediately was then stirred at room temperature for an hour. The resultant suspension was refluxed for 2 hour. The resulting solid product was then filtered off and air-dried (95% yields).

Results and Discussion

As reported in our earlier communication, the polyureas (PUs) formation is performed by facile reaction of $-NH_2$ group's moiety with –NCO groups. All PUs are found to be colored powders. They do not melt up to 250°C and are insoluble in common organic solvents. (C, H, N, S) (Table 1) of each of the PUs are consistent with the corresponding predicted structure (reaction scheme).

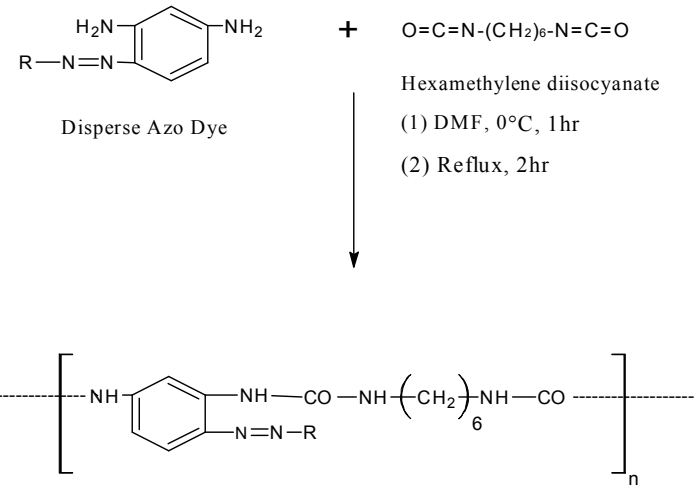

Figure 1 Synthesis Steps

Where R=

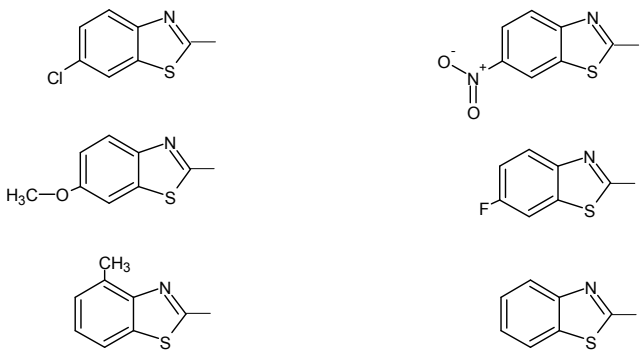

TABLE 1 Characterization of Polyureas (PUs)

PU Sample	Mole Formula of Repeating Unit	Mol. Wt. of Repeating Unit	$\overline{Mn}$	Elemental Analysis			
				%C Found (Calcd.)	%H Found (Calcd.)	%N Found (Calcd.)	%S Found (Calcd.)
PU-1	$C_{21}H_{22}ClN_7O_2S$	473	3784	53.10 (53.28)	4.50 (4.65)	20.60 (20.72)	6.50(6.77)
PU-2	$C_{22}H_{25}N_7O_3S$	469	4690	56.20 (56.29)	5.30 (5.33)	20.70 (20.90)	6.80 (6.82)
PU-3	$C_{22}H_{25}N_7O_2S$	453	4530	58.10 (58.28)	5.40 (5.52)	21.60 (21.63)	6.80 (7.06)
PU-4	$C_{21}H_{22}N_8O_4S$	484	3388	52.00 (52.07)	4.50 (4.55)	23.10 (23.14)	6.30 (6.61)
PU-5	$C_{21}H_{22}FN_7O_2S$	457	3656	55.00 (55.14)	4.60 (4.81)	21.30 (21.44)	6.90 (7.00)
PU-6	$C_{21}H_{23}N_7O_2S$	439	3942	57.30 (57.40)	5.20 (5.24)	22.30 (22.32)	7.00 (7.29)

TABLE 2 TGA of PUs

PU Samples	**% wt. loss at various temperature °C from TGA**					
	200	300	400	500	600	700
PU-1	2.1	6.9	22.6	65.2	75.9	77.3
PU-2	2.5	7.9	20.1	67.6	74.2	78.8
PU-3	2.9	8.1	21.3	68.1	74.8	79.5
PU-4	2.0	7.7	24.6	63.9	75.1	76.9
PU-5	2.7	8.3	21.6	68.2	76.2	78.6
PU-6	2.8	7.6	23.8	64.8	75.6	78.1

IR spectra of all the PUs are identical in almost all aspects and inspection of all the spectra reveals that the spectra comprise important IR spectral features of urea linkages. The IR bends at 1620-1280 cm^{-1}, 1240-1250 cm^{-1} may be respectively due to urea linkage. The other IR spectra features are due to aromatic and aliphatic segments of monomers and appear at their expected positions.

As the produced polymers are insoluble in organic solvents, the colligative properties (i.e. viscosity, osmometry) have not been studied and hence the number average molecular weight $\overline{Mn}$ of all the polymer samples have been measured by end group – NH_2 by non-aqueous conductometric titration. The results of $\overline{Mn}$ values are furnished in Table 1.

TG data of PUs are shown in Table 2. Inspection of the TG thermograms reveals that all the PUs decomposed in one step. They start their degradation about 200°C, and lose their weight rapidly between 200 to 600°C.

Conclusion

The present work is colored polyureas. The nature of theses polymer is amorphous colored powder. They have good thermal stability. Having urea groups they can compatible to the thermoplast and can be easily form the colored article even though article processed at high temperature. Looking to the properties of colored polyureas they can not be bloom or bleed from the articles.

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