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## Preparation of novel dye copolymers based on 4-[4-(2-Hydroxy-1-naphthyl azo)phenyl]-1,2,4-triazolidine-3,5-dione

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### ABSTRACT

The reaction of 4-(4-nitrophenyl)urazole (1) with two moles of hexamethylene diisocyanate (HMDI) in dimethylformamide (DMF) to produce new diisocyanate(2). The products were reacted with 4-(4-aminophenyl) urazole -  $\beta$ -naphthol without separation to producing novel dye copolymers, with relatively good inherent viscosities. These novel copolymers have inherent viscosities in a range of 0.25 - 0.31 dLg<sup>-1</sup> in DMF at 25°C. Some structural characterization and physical properties of these novel copolymers are reported. © 2013 Trade Science Inc. - INDIA

### KEYWORDS

4-(4-nitrophenyl)urazole;  
4-(4-aminophenyl) urazole -  
 $\beta$ -naphthol;  
Copolymers;  
Inherent viscosity.

### INTRODUCTION

The Design and synthesis of bi-functional colorants has received considerable attention because such colorants can be utilized as monomers for functional polymers via polyaddition and polycondensation reactions<sup>[1]</sup>. Owing to the inherent non-leaching behavior and good light fastness combined with the special properties of polymers<sup>[2,3]</sup>, there has been much emphasis given to the synthesis of polymers containing chromophoric groups<sup>[4,5]</sup>, for example, the aromatic azo group which can form the part of the main chain. In addition, the aromatic azo group is of special interest because of the existence of cis-trans isomerism and its effect on the photochromic properties of the polymers. Therefore, polymers that contain the azo group have potential use in a variety of applications<sup>[6]</sup>, such as materials with liquid-crystal<sup>[7,8]</sup> or non-linear optic properties<sup>[9]</sup>. Azobenzene-containing materials are photo

chromic and reversibly switch between two spectroscopically distinct forms by use of light. Thus azobenzene-based polymers are interesting due to their photo responsive behavior which can be utilized in optical switches, optical data recording or optical information storage<sup>[10-12]</sup>. Urazoles (1,2,4-triazolidine-3,5-diones) are very significant chemical reagents in the laboratory as well as in industry. Industrially urazoles are used as a stabilizer in milk, and in the production of anti-tumor drugs<sup>[13]</sup>. They are also utilized in polymeric materials<sup>[14,15]</sup>, in the production of automobile air bags, as a blowing agent in plastics, in the manufacture of antifungal compounds, and herbicides<sup>[16]</sup>. Urazoles have been used as a laboratory reagent for preparation of novel organometallic and heterocyclic compounds<sup>[17]</sup>; for example triazolo[1,2-a]indazole-triones have been prepared via a three-component method, by using homogeneous<sup>[18]</sup>, or heterogeneous<sup>[19]</sup> catalysts. Some urazole derivatives were found to be potent cytotoxic agents in

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murrain and human cancer cell lines. Other pharmaceutical properties of urazole derivatives are hypolipidemic activity via lowering serum, cholesterol, and triglyceride levels<sup>[20]</sup>, pesticides<sup>[21]</sup> and insecticides<sup>[22]</sup>. Preparations of thermoplastics, production of heat resistant coatings<sup>[23]</sup>, tire rubbers with high gripability<sup>[24]</sup> and melamine resins<sup>[25]</sup>, are among the applications in the field of polymerization of urazole derivatives. The synthesis and characterization of the macromolecules restrain heterocyclic rings in the main chain has been the topic of considerable interest, because of their relatively good thermal stability and some attractive novel properties<sup>[26]</sup>.

## EXPERIMENTAL

### Apparatus

IR spectra were recorded on Shimadzu 470 IR spectrophotometer. Spectra of solids were carried out using KBr disks. Vibrational transition frequencies are reported in wave number ( $\text{cm}^{-1}$ ). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fensk Routine Viscometer. Thermal gravimetric analysis (TGA) data for polymers were taken by Amir-Kabir University, Tehran, Iran, in nitrogen atmosphere at a rate of  $10^\circ\text{C}/\text{min}$ .

### Reagents and monomer

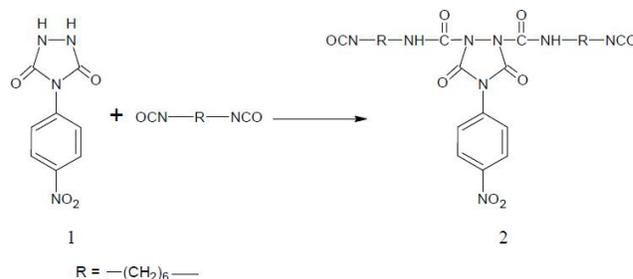
Reagents were purchased from Fluka Chemical Co., Aldrich Chemical Co. and Merk Co. 4-(4-nitrophenyl)-urazole was synthesized according to our previous report<sup>[27]</sup>.

### Synthesis of 4-(4-nitrophenyl)-urazoldiisocyanate

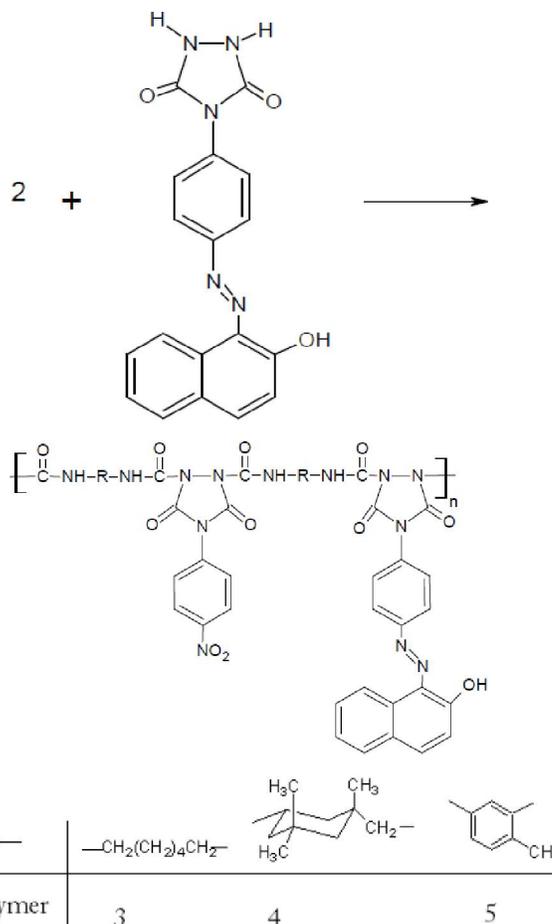
The reaction of 4-(4-nitrophenyl)-Urazole with hexamethylenediisocyanate.

In a 25 mL round bottom flask, was placed 4-(4-nitrophenyl)-Urazole (0.164 g,  $7.37 \times 10^{-3}$  mol), hexamethylenediisocyanate (0.248 g,  $1.47 \times 10^{-3}$  mol) and 2 mmol DMF as solvent. The reaction mixture was stirred for 2 days at room temperature, then the solution pured in 50 mL  $\text{CCl}_4$ . The yellow solid was filtrated off, and washed with hot ethanol. (0.35 g, 86%). mp  $152^\circ\text{C}$ .

IR (KBr): 3350 (w), 3105 (w), 2920(s), 2850(m), 2275(s), 1790 (m), 1750 (s, br), 1670(m, br), 1620(m), 1580 (m), 1520(m), 1415 (m), 1350 (s), 1250 (m), 1210(m), 1155 (w), 1060 (m), 1015 (w), 855 (m), 825(w), 750 (m, sh), 680 – 540(m, br)  $\text{cm}^{-1}$ .



Scheme 1 : Preparation of 4-(4-nitrophenyl)-urazoldiisocyanate



Scheme 2 : Preparation of copolymers

### Polymerization of 4-(4-nitrophenyl)-urazole with hexamethylene diisocyanate

In a 10 mL round bottom flask, 4-(4-nitrophenyl)-urazoldiisocyanate, 4-[4-(2-hydroxy-1-naphthyl azo)phenyl]-1,2,4-triazolidine-3,5-dione and N,N-

dimethylformamide (DMF) as solvent was added. The solution was stirred for 24 h at room temperature. 0.5 mL of DMF was added and the solution was stirred for 24 h in 70 °C, then for 24 h in 90 °C. The viscose gel was precipitated in 50 mL of methanol. The yellow solid was filtrated and dried.

## RESULTS AND DISCUSSION

### Monomer synthesis

4-(4-nitrophenyl)-urazole was reacted with 2 mol of hexamethylenediisocyanate in DMF as solvent at room temperature Scheme 1. The compound was characterized by IR. The IR spectrum showed a peak at 3350  $\text{cm}^{-1}$  for the stretching vibration of the N-H bonds, and a peak at 3105  $\text{cm}^{-1}$  for the stretching vibration of the aromatic C-H bonds. The strong peak at 1750  $\text{cm}^{-1}$  covers the carbonyl related area of both the urazolic and the imidic carbonyl groups. The strong peak at 1520 is related to stretching vibrations of the aromatic carbon-carbon double bonds.

### Polymerization reactions

Since various derivatives of 1,2,4-triazolidine-3,5-dione have been reacted with aliphatic and aromatic diisocyanates to produce related polymers<sup>[28]</sup>, we decided to perform this type of reaction for the formation of the novel nitrophenyl urazole containing dye-copolymers. The reaction of monomer with this 4-[4-(2-hydroxy-1-naphthylazo)phenyl]-1,2,4-triazolidine-3,5-dione was performed via solution polymerization. The reactions were carried out in DMF solution and the resulted polyureas(3-5) were obtained as yellow solids in high yields Scheme 2. The resulting copolymers were characterized by IR and TGA.

The IR spectrum of the polymer (3) showed a peak at 3290  $\text{cm}^{-1}$  for stretching vibration of the amide N-H bounds, a peaks at 3025  $\text{cm}^{-1}$  for stretching vibration of the aromatic. The peaks at 1765, 1720  $\text{cm}^{-1}$  and 1700  $\text{cm}^{-1}$  are the specific characteristic of the urazolic carbonyls which covers the main chain carbonyl groups. The strong peak at 1500 and 1300  $\text{cm}^{-1}$  is also related to stretching vibrations of nitro groups.

The IR spectrum of the polymer (4) showed a peak at 3310  $\text{cm}^{-1}$  for stretching vibration of the amide N-H and OH bounds. The peak appeared at 2970 is

attributed to stretching vibration of the aliphatic C-H bounds. The peaks at 1780, 1720  $\text{cm}^{-1}$  are the specific characteristic of the urazolic carbonyls which covers the main chain carbonyl groups. The strong peak at 1620 is related to stretching vibrations of N-H bond. The peak at 1500 is related to aromatic carbon-carbon double bonds. The peaks at 1540 and 1335  $\text{cm}^{-1}$  is also related to stretching vibrations of nitro groups.

The IR spectrum of the polymer (5) showed a peak at 3290  $\text{cm}^{-1}$  for stretching vibration of the N-H bound. The peak appeared 2900  $\text{cm}^{-1}$  is attributed to stretching vibration of the aliphatic C-H bounds of the tolylene groups. The peaks at 1700 and 1640  $\text{cm}^{-1}$  are the specific characteristic of the urazolic carbonyls which covers the main chain carbonyl groups. Also the strong peak at 1540 and 1420  $\text{cm}^{-1}$  is attributed to stretching vibrations of the aromatic carbon-carbon double bonds.

The copolymers (3), (4) and (5) are soluble in polar organic solvents such as DMF, DMSO and DMAc, and are insoluble in solvents such as water, methanol, acetone, cyclohexane and chloroform.

### Thermal properties

The thermal behavior of the copolymers 3, 4 and 5 was measured by thermogravimetric analysis (TGA) at a rate of 10 °C/min in nitrogen atmosphere. The copolymer 3 shows 5% and 10% weight loss at 183 and 188 °C respectively and 0 % residual weight at 600 °C. The polymer 4 shows 5% weight loss at 170 °C and 10% weight loss at 223 °C and 60 % weight loss at 600 °C. Also an examination of the data for the polymer 9 shows that this copolymer shows 5% and 10% weight loss at 56 and 100 °C respectively and 0 % at 600 °C. These are depend on their chemical structures of copolymers.

## CONCLUSIONS

This investigation has shown that 4-(4-nitrophenyl)-urazole diisocyanate is an interesting monomer for the polycondensation reactions for preparation of copolymers. This compound can act as a bifunctional monomer and its polymerization reaction with another compound gave the novel dye copolymers(3-5).

## Full Paper

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