



Synthesis and Characterization of Polyurethanes of Isophorone Diisocyanate Containing *Bis*(azo) and *Bis*(*o*-Nitrobenzyl) Chromophores in the Main Chain

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A series of photosensitive polyurethanes containing *bis*(azo) and *bis*(*o*-nitrobenzyl) groups were synthesized by polyaddition reactions of diols such as *bis*(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane, 4-hydroxy-3-methylphenylazo-4'-hydroxy-phenylazo-2,2'-dinitrodiphenylmethane and *bis*(4-hydroxy-3-methylphenylazo)-2,2'-dinitro-diphenylmethane with isophorone diisocyanate, in dimethyl acetamide in presence of di-*n*-butyltin dilaurate as catalyst. All of them were characterized by IR, UV-vis, ¹H and ¹³C NMR spectra and also by differential scanning calorimetry and gel permeation chromatography.

Key Words: Photosensitive polyurethanes, *Bis*(azo), *Bis*(*o*-nitrobenzyl).

INTRODUCTION

Polyurethanes with chromophore structures attached to the polymeric chains have attracted great interest in recent years because of the possibility of a broad range of applications. The azobenzene bearing polyurethanes in particular, are predicted to be of use in the field of non-linear optics¹, optical data storage or processing^{2,3} and biomedical goods⁴. The incorporation of photochemically active units into the polymeric backbone to obtain photoactive materials is a valid alternative to doping with low molecular weight chromophores^{5,6}.

Generally, polyurethanes are formed either by the reaction of *bis*chloroformate with a diamine or by the reaction of a diisocyanate with a diol⁷⁻⁹. The diisocyanate-diol method has the advantage over *bis*chloroformate-diamine method in that it involves a simple addition reaction without any by-product formation. The chemistry of the formation of various polyurethanes has been reviewed by several researchers using different starting materials^{10,11}. The present paper describes the synthesis and characterization of polyurethanes of isophorone diisocyanate (IPDI) with diols such as *bis*(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane, 4-hydroxy-3-methylphenylazo-4'-hydroxy-phenylazo-2,2'-dinitrodiphenylmethane and *bis*(4-hydroxy-3-methylphenylazo)-2,2'-dinitrodiphenyl-methane.

EXPERIMENTAL

Isophorone diisocyanate (Fluka) and the catalyst, di-*n*-butyltin dilaurate (Fluka) were used as received without purification. Solvents such as dimethyl acetamide, dioxane and

methanol (E. Merck) were purified by standard procedures. The diols were purified by column chromatography using 100-200 mesh silica gel and appropriate mixture of benzene and ethyl acetate-benzene mixture for elution. The solvents were distilled before use for column chromatography. The purity of the crude and recrystallized products was monitored both by UV and TLC measurements. TLC was performed on glass plate coated with silica gel GF254 containing 13 % calcium sulphate as binder. Appropriate solvents were used for development and the developed plates were visualized by exposure to iodine. Spectroscopic grade solvents were used for all measurements.

IR spectra were recorded on IFS 66U FTIR spectrometer. ¹H NMR spectra were recorded on Jeol model GSX 400 MHz spectrometer and ¹³C NMR spectra were obtained using Bruker 300 MHz spectrometer with TMS as internal standard. UV-Vis-spectra were obtained using Shimadzu UV-2100 spectrophotometer. DSC measurements were performed on a NETZSCH DSC 204 instrument in an atmosphere of nitrogen, at a heating rate of 10 °C/min and the temperature range was 20-500 °C. The weight average and number average molecular weights (\bar{M}_w and \bar{M}_n) of the polyurethanes were determined using Waters 590 gel permeation chromatograph equipped with four ultragel columns (500, 10³, 10⁴, 10⁵ Å) and calibrated with polystyrene standards with molecular weights of 1.024 × 10³ to 3.9 × 10⁶ g mol⁻¹. Universal calibration was performed with Mark-Houwink-Sakura polyurethane constants: K = 2.9 × 10⁻⁴ dL g⁻¹ and a = 0.70^{12,13}. Dimethyl acetamide was used as the eluent and a flow rate of 1 mL/min was maintained in all runs.

Synthesis of monomers: The aromatic diols for polyurethane synthesis were prepared as per the **Scheme-I**. The monomers used are (i) *bis*(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane, [**1c**] (ii) 4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2,2'-dinitrodiphenylmethane, [**1d**] (iii) *bis*(4-hydroxy-3-methylphenylazo)-2,2'-dinitrodiphenylmethane, [**1e**] and (iv) isophorone diisocyanate.

Synthesis of polyurethanes based on isophorone diisocyanate

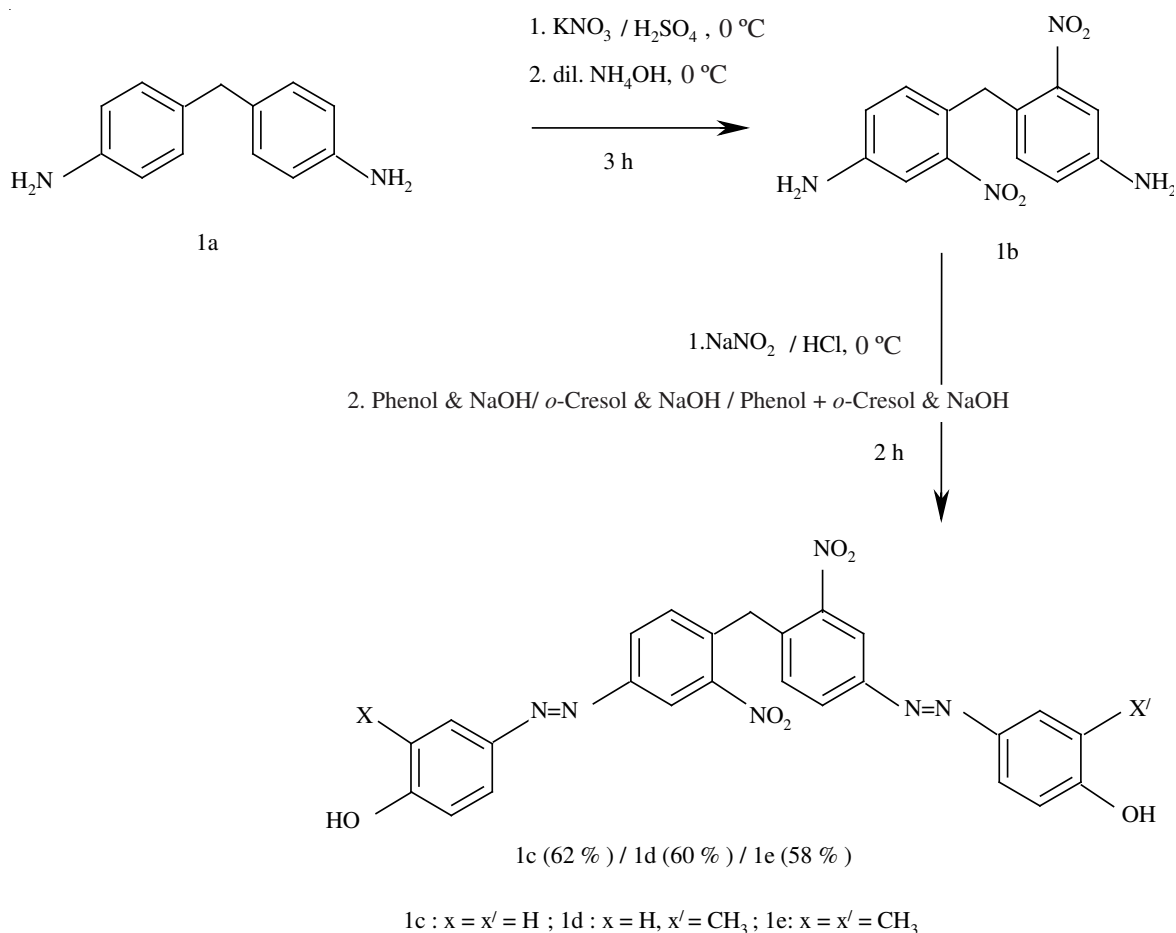
Polyurethane of isophorone diisocyanate and *bis*(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane (PU 1a): Poly[5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane-co-*bis*(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane].

A solution of *bis*(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane (6 mmol, 2.988 g) in HPLC grade dimethyl acetamide (50 mL) was stirred in a flame-dried round bottom flask of 500 mL capacity, equipped with a magnetic stirring bar, nitrogen inlet, a thermometer and a reflux condenser with a CaCl₂ guard-tube. To this, a slight excess of a solution of isophorone diisocyanate (6.3 mmol, 1.3 mL) in dimethyl acetamide (10 mL) and di-*n*-butyltin dilaurate (4 drops) were added with vigorous stirring. The stirring was continued at room temperature for *ca.* 10 min and the mixture was then heated at 70 °C for 20 h and cooled to room temperature. The viscous reaction mixture obtained was poured into 500 mL of

water with stirring. The solid polymer obtained was separated, washed with methanol to remove the catalyst, dimethyl acetamide and leachable oligomers, if any. The polymer was then dried under vacuum for 6 h. Yellowish-brown solid was obtained.

Yield: (76 %), IR (KBr, ν_{\max} , cm⁻¹): 3368 [N-H]; 2923 [-CH₂-]; 1703 [urethane carbonyl]; 1618 [-N=N-]; 1533, 1350 [-NO₂]; 1238 [-C-O-C in -COOC- of PU], UV (dioxane, λ_{\max} , nm): 370 [$\pi \rightarrow \pi^*$, -N=N-]; 248 [$n \rightarrow \pi^*$, -NO₂], ¹H NMR (DMSO-*d*₆, δ): 8.47 [4H (d), phenyl]; 8.15 [4H (d), phenyl]; 8.77 [2H (s), phenyl]; 8.2 [2H (d), phenyl]; 8 [2H (d), phenyl]; 7 [2H (m), -OCONH-]; 2.95 [2H (s), Ph-CH₂-Ph]; 0.875, 0.9, 1 [CH₃ of IPDI]; 1.25, 1.95, 2.1 [CH₂ of IPDI]; 2.78 [CH₂, of IPDI]; 3.5 [CH of IPDI], ¹³C NMR (DMSO-*d*₆, δ): 32 [methylene]; 121, 125, 127, 135, 137, 139, 144, 152, 153, 170 [aromatic]; 23.1, 27.5, 35 [CH₃ of IPDI]; 36.2 [CH of IPDI]; 36.4 [-C- of IPDI]; 31.7 [-C(CH₃)₂- of IPDI]; 41.4, 46.2, 46.7 [CH₂ of IPDI]; 56 [CH₂ of IPDI]; 156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl carbon of IPDI].

Polyurethane of isophorone diisocyanate and 4-hydroxy-3-methyl phenylazo-4'-hydroxyphenylazo-2,2'-dinitrodiphenylmethane (PU 1b): Poly[5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane-co-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2,2'-dinitrodiphenylmethane].



Scheme-I

A solution of 4-hydroxy-3-methylphenylazo-4'-hydroxy-phenylazo-2,2'-dinitrodiphenyl methane (6 mmol, 3.072 g) in HPLC grade dimethyl acetamide (50 mL) was stirred in a 500 mL round bottom flask, equipped with nitrogen gas inlet, a magnetic stirrer, a thermometer and a reflux condenser with a CaCl₂ guard-tube. To this, a solution of isophorone diisocyanate (6.3 mmol, 1.3 mL) in dimethyl acetamide (10 mL) and di-*n*-butyltin dilaurate (4 drops) were added and the mixture was heated at 70 °C for 20 h, with stirring. The viscous reaction mixture was then cooled to room temperature and was poured into excess of water with stirring. The precipitated polymer was separated, washed with methanol and dried under vacuum. Orange-yellow solid was obtained.

Yield: 80 %, IR (KBr, ν_{\max} , cm⁻¹): 3319 [N-H]; 2924 [-CH₂]; 1710 [urethane carbonyl]; 1597 [-N=N-]; 1531, 1350 [-NO₂]; 1241 [-C-O-C in -COOC- of PU], UV (dioxane, λ_{\max} , nm): 376 ($\pi \rightarrow \pi^*$, -N=N-); 246 ($n \rightarrow \pi^*$, -NO₂), ¹H NMR (DMSO-*d*₆, δ): 8.77 [2H (s), phenyl]; 8.2 [2H (d), phenyl]; 8 [2H (d), phenyl]; 8.47 [2H (d), phenyl]; 8.15 [2H (d), phenyl]; 8.37 [1H (d), phenyl]; 8.1 [1H (d), phenyl]; 8.05 [1H (s), phenyl]; 7 [2H (m), -OCONH-]; 2.95 [2H (s), Ph -CH₂-Ph]; 2.29 [3H (s), CH₃]; 0.875, 0.9, 1 [CH₃ of IPDI]; 1.25, 1.95, 2.1 [CH₂ of IPDI]; 2.78 [CH₂ of IPDI]; 3.5 [CH of IPDI], ¹³C NMR (DMSO-*d*₆, δ): 20 (methyl); 32 [methylene]; 122, 126, 128, 130, 132, 135, 138, 146, 148, 151, 152, 153, 170 [aromatic]; 23.1, 27.5, 35 [CH₃ of IPDI]; 36.2 [CH of IPDI]; 36.4 [-C- of IPDI]; 31.7 [-C(CH₃)₂- of IPDI]; 41.4, 46.2, 46.7 [CH₂ of IPDI]; 56 [CH₂ of IPDI]; 156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl carbon of IPDI].

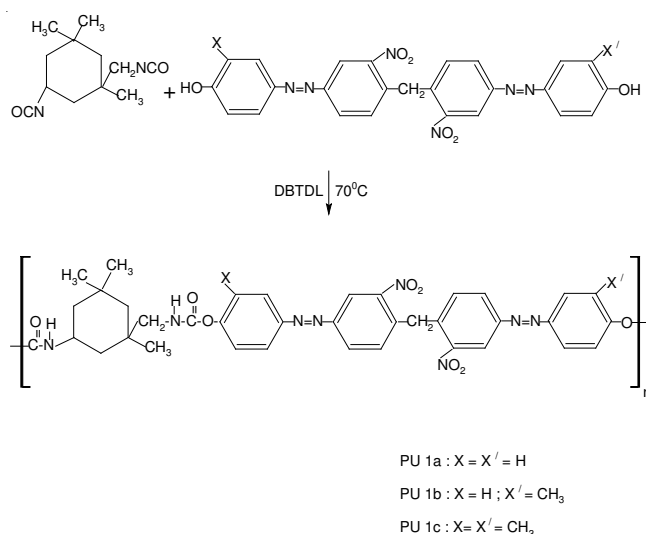
Polyurethane of isophorone diisocyanate and bis(4-hydroxy-3-methylphenylazo)-2,2'-dinitrodiphenylmethane (PU 1c): Poly[5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane-co-bis(4-hydroxy-3-methylphenylazo)-2,2'-dinitrodiphenylmethane].

To a solution of bis(4-hydroxy-3-methylphenylazo)-2,2'-dinitrodiphenylmethane (4.5 mmol, 2.37 g) in HPLC grade dimethyl acetamide (40 mL), isophorone diisocyanate (4.95 mmol, 1.05 mL) in dimethyl acetamide (10 mL) and di-*n*-butyltin dilaurate (3 drops) were added and the resulting mixture was stirred for 20 h at 70 °C. The reaction mixture was then added to large excess of water to precipitate the polyurethane formed. The polymer was filtered, washed with methanol and dried under vacuum. Orange-yellow solid was obtained.

Yield: 84 %, IR (KBr, ν_{\max} , cm⁻¹): 3332 [N-H]; 2924 [-CH₂-]; 1725 [urethane carbonyl]; 1620 [-N=N-]; 1532, 1352 [-NO₂]; 1244 [-C-O-C in -COOC- of PU], UV (dioxane, λ_{\max} , nm): 379 [$\pi \rightarrow \pi^*$, -N=N-]; 253 [$n \rightarrow \pi^*$, -NO₂], ¹H NMR (DMSO-*d*₆, δ): 8.77 [2H (s), phenyl]; 8.2 [2H (d), phenyl]; 8 [2H (d), phenyl]; 8.37 [2H (d), phenyl]; 8.1 [2H (d), phenyl]; 8.05 [2H (s), phenyl]; 7 [2H (m), -OCONH-]; 2.95 [2H (s), Ph-CH₂-Ph]; 2.29 [6H (s), two CH₃]; 0.875, 0.9, 1 [CH₃ of IPDI]; 1.25, 1.95, 2.1 [CH₂ of IPDI]; 2.78 [CH₂ of IPDI]; 3.5 [CH of IPDI], ¹³C NMR (DMSO-*d*₆, δ): 20(methyl); 32 [methylene]; 122, 128, 130, 131, 135, 137, 139, 146, 152, 154, 170 [aromatic]; 23.1, 27.5, 35 [CH₃ of IPDI]; 36.2 [CH of IPDI]; 36.4 [-C- of IPDI]; 31.7 [-C(CH₃)₂- of IPDI]; 41.4, 46.2, 46.7 [CH₂ of IPDI]; 56 [CH₂ of IPDI]; 156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl carbon of IPDI].

RESULTS AND DISCUSSION

The synthetic route leading to the polyurethane obtained from isophorone diisocyanate and the diol is shown in **Scheme-II**. The IR spectrum of the polyurethanes PU1a, PU1b and PU1c showed characteristic strong absorption bands at 3368, 3319, 3332 cm⁻¹, respectively due to the hydrogen bonded N-H stretching vibration and at 1703, 1710 and 1725 cm⁻¹, respectively due to carbonyl stretching vibration of the urethane bond. The absorption band at ca. 1530 cm⁻¹ is due to the C-N-H bending of the urethane group and the asymmetric stretching of aromatic C-NO₂. Absorption bands due to CH₂-stretching at ca. 2924 cm⁻¹, NO₂ group at ca. 1530 and ca. 1350 cm⁻¹, azo group at 1618, 1597, 1620 cm⁻¹, respectively and C-O-C stretching of urethane at 1238, 1241 and 1244 cm⁻¹, respectively were also observed.



Scheme-II: Synthetic route for the polyurethanes **PU1a**, **PU1b**, **PU1c** from IPDI and **1c**, **1d**, **1e**

In the UV spectra of the above polyurethanes, absorption due to $n \rightarrow \pi^*$ of the -NO₂ group occurred at 248, 246 and 253 nm and the absorption due to $\pi \rightarrow \pi^*$ of the azo group occurred at 370, 376 and 379 nm, respectively. However, the absorption due to the urethane carbonyl could not be observed, it might be due to either overlapping between carbonyl and the nitro absorption or shortening of the absorption wavelength.

The ¹H NMR spectra of the polymers based on isophorone diisocyanate confirmed that the peak at δ 7 was due to NH proton of the urethane linkage. The aromatic protons showed peaks between δ 8.77 and 8. The peak at δ 2.95 was due to methylene protons of Ph-CH₂-Ph. The peaks at δ 0.875, 0.9, 1.0, 1.25, 1.95, 2.1, 2.78 and 3.5 were due to the protons of isophorone diisocyanate.

In the ¹³C NMR spectra of the polymers, the urethane carbonyl carbon gave resonance signals at δ 156.4 and 158.2 due to the primary and secondary urethane carbonyl carbon of IPDI. The signals between δ 23.1 and 56 were due to carbons of IPDI. The signal at δ 32 was due to the methylene carbon of Ph-CH₂-Ph. The signals due to aromatic carbons were between δ 121-170.

The polyurethanes **PU1a**, **PU1b** and **PU1c** showed glass transition temperature at 160, 165 and 170 °C and melting

points at 295, 300 and 304 °C, respectively. The increase in T_g and T_m values from **PU1a**, **PU1b** to **PU1c** indicates that with increase in the number of electron releasing methyl substituent at the diol component of the polyurethane, the strength of the urethane bond increases. The average molecular weights of the polymers were determined by GPC. \overline{M}_n and \overline{M}_w of **PU1a** were 12560 and 24452, that of **PU1b** were 12574 and 24466 and that of **PU1c** were 12588 and 24480, respectively, with a polydispersity index of ca. 1.94.

Conclusion

The polyurethanes thus synthesized from aromatic diols containing *bis*(azo) and *o*-nitrobenzyl chromophores with IPDI can be used for the study of the photochemistry of nitro groups and urethane bond in a constrained environment of azo-groups in the polymer. They may also have liquid crystalline properties because of the presence of azo groups, nitro groups and the rigidity due to the double bond character of the amide group coupled with extensive hydrogen bonding.

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REFERENCES

- (a) O. Watanabe, M. Tsuchimori and A. Okada, *J. Mater. Chem.*, **6**, 1487 (1996); (b) E. Jecs, J. Kreicberga, V. Kampars, A. Jurgis and M. Rutkis, *Optical Mater.*, **31**, 1600 (2009).
- Y. Liu and G.O. Carlisle, *J. Mater. Sci. Lett.*, **16**, 642 (1997).
- (a) M. Brecl and T.J. Malavasic, *J. Polym. Sci. A: Polym. Chem.*, **35**, 2871 (1997); (b) M.N. Rhyner, A.M. Smith, X. Gao, H. Mao, L. Yang and S. Nie, *Nanomedicine*, **1**, 209 (2006).
- (a) P. David and S. Rasmane, *Polym. Prep.*, **38**, 598 (1997); (b) Y.-P. Tian, L. Li, J.-Z. Zhang, J.-X. Yang, H.-P. Zhou, J.-Y. Wu, P.-P. Sun, L.-M. Tao, Y.-Y. Guo, C.-K. Wang, H. Xing, W.-H. Huang, X.-T. Tao and M.-H. Jiang, *J. Mater. Chem.*, **17**, 3646 (2007).
- J. Camerin, C.G. Wilson and J. Frechet, *J. Am. Chem. Soc.*, **118**, 12925 (1996).
- H. Ziam-Cherif, K. Lamachi and T. Matsuda, *Macromolecules*, **32**, 3438 (1999).
- D. Bose, *Macromol. Chem. Macromol. Symp.*, **50**, 91 (1991).
- F. Papadimitrakopoulos, *Polym. Prepr.*, **31**, 486 (1990).
- Z.S. Petrovic, M. Ilavsky, K. Dusek, M. Vidacovic, I. Javim and B. Banjamin, *J. Appl. Polym. Soc.*, **42**, 391 (1991).
- T.M. Santosusso, *Rubber Plast. News*, **20**, 13 (1990).
- R.F. Harris, C.D. Deprter and R.B. Potler, *Macromolecules*, **24**, 2973 (1991).
- K.W. Krueger, *Angew. Makromol. Chem.*, **26**, 47 (1972).
- D.C. Lee, T.A. Speckhard, A.D. Sorensen and S.L. Cooper, *Macromolecules*, **19**, 2383 (1986).