Photolysis of Polyurethanes

5.1 Introduction

Polyurethanes are well-known for their widespread applications due to their excellent physical properties. The properties of these polymers can be modified considerably by incorporating various functional groups. Most research on photolysis of polyurethanes is centered on the effect of the structure of aromatic diisocyanates. So far only a very few investigations were carried out on the effect of structure of aromatic diols on the photolysis of polyurethanes. So for the present work, the photo-restructuring of polyurethanes containing 2-nitrobenzyl and azo chromophores in the main chain is studied with a view to evaluate the feasibility of using them as photoresist formulations and as information storage systems. Photolysis of the synthesized polyurethanes resulted in o-photo-Fries rearrangement at the urethane part without degradation, in the case of TDI based polyurethanes, whereas, there was no change at the urethane bond in IPDI and HMDI based polyurethanes, involving trans-cis-trans cycle at the azo group and a redox reaction at one of the o-nitrobenzyl groups of the polymer. As a consequence of this, a differential polarity is developed in the molecule and correspondingly a solubility difference is observed between the polymer and the irradiated polymer. Thus, the possibility of using the polyurethanes as photoresists is established. Also, the trans-cis-trans cycle observation revealed the possibility of using them as optical information storage systems.
5.2 Experimental

5.2.1 Materials and Methods

Irradiations were carried out with a Philips HPK 125W high pressure mercury lamp in a water-cooled quartz reactor. UV-Vis spectra were recorded on a Schimadzu UV-2100 spectrophotometer. IR spectra were recorded on IFS 66U model FTIR spectrometer. $^1$H NMR and $^{13}$C NMR spectra were obtained using Bruker 300 MHz spectrometer with TMS as internal standard. Thin-layer chromatography was carried out on silica gel plates (Merck GF254).

Photolysis of the polyurethanes was carried out in isopropanol and ethyl acetate under acidic and neutral conditions. The solvents in this study were either dried or freshly distilled before use.

5.2.2 Photolysis of Polyurethanes based on IPDI

5.2.2.1 Photolysis of Polyurethanes (PU1a / PU1b / PU1c) based on Isophorone diisocyanate and 2c / 2d/ 2e in neutral 2-propanol

A solution of the polyurethane (PU1a / PU1b / PU1c, 500 mg) in pure dry 2-propanol (1000 mL) was deoxygenated by bubbling nitrogen gas for 20 minutes. The stirred solution was irradiated in a water-cooled photoreactor for 23 h, using a high pressure mercury vapour lamp. The UV-Vis absorption readings of the solution were recorded before irradiation and after irradiation at regular intervals of time. Typically, the results for PU1a are given in Table 5.1. The corresponding UV-Vis absorption curves are shown in fig 5.1a. After 23 h of irradiation, TLC examination of the solution showed the absence of the starting material. The solvent was removed by distillation under reduced pressure. The residue photoproduct was identified as PU2a / PU2b / PU2c corresponding to PU1a /
Table 5.1 Variation of $\lambda_{\text{max}}$ and absorbance with UV exposure time of Polyurethane of IPDI and Bis (4-hydroxyphenylazo)-2, 2'-dinitrodiphenylmethane (PU1a) in 2-propanol

<table>
<thead>
<tr>
<th>Time of UV exposure (in hours)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>378; 250</td>
<td>0.440; 0.329</td>
</tr>
<tr>
<td>4</td>
<td>376; 250</td>
<td>0.386; 0.15</td>
</tr>
<tr>
<td>9</td>
<td>378; 230</td>
<td>0.323; 0.199</td>
</tr>
<tr>
<td>15</td>
<td>378; 228</td>
<td>0.374; 0.241</td>
</tr>
<tr>
<td>23</td>
<td>378; 248</td>
<td>0.404; 0.271</td>
</tr>
</tbody>
</table>

Table 5.2 $\lambda_{\text{max}}$ of polyurethanes before irradiation and their photoproducts in dioxane

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>$\lambda_{\text{max}}$(nm)</th>
<th>Absorbance</th>
<th>Photoproduct</th>
<th>$\lambda_{\text{max}}$(nm)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU1a</td>
<td>370</td>
<td>0.473</td>
<td>PU2a</td>
<td>364</td>
<td>0.729</td>
</tr>
<tr>
<td></td>
<td>248</td>
<td>0.353</td>
<td></td>
<td>246</td>
<td>0.214</td>
</tr>
<tr>
<td>PU1b</td>
<td>376</td>
<td>0.626</td>
<td>PU2b</td>
<td>374</td>
<td>0.597</td>
</tr>
<tr>
<td></td>
<td>246</td>
<td>0.451</td>
<td></td>
<td>248</td>
<td>0.518</td>
</tr>
<tr>
<td>PU1c</td>
<td>379</td>
<td>1.438</td>
<td>PU2c</td>
<td>376</td>
<td>0.535</td>
</tr>
<tr>
<td></td>
<td>253</td>
<td>1.037</td>
<td></td>
<td>252</td>
<td>0.458</td>
</tr>
</tbody>
</table>
PUlb / PUlc respectively, on the basis of spectral data. Typically, the effect of UV irradiation on the absorption spectrum of PU1a in dioxane before and after irradiation is also given in fig 5.1b.

Fig 5.1a UV curves of PU1a in 2-propanol at different time intervals: a = 0 h, b = after 4 h, c = 9 h, d = 15 h, e = 23 h.

Fig 5.1b Effect of UV irradiation on the absorption spectrum of PU1a in dioxane (a) before irradiation and (b) after irradiation
5.2.2.2 Photoproduct of PU1a: Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylcyclohexane –co- cis-bis (4-hydroxyphenylazo)-2-nitro-2'-nitrosodiphenyl carbinol]: PU2a

IR (KBr, cm\(^{-1}\)): 3408 [-OH / N-H]; 2923 [-CH-]; 1703 [urethane carbonyl]; 1585 [-N = N-]; 1534, 1349 [-NO\(_2\)]; 1504 [nitroso]; 1238 [-C-O-C in –COOC- of PU]

UV (dioxane, \(\lambda_{max}\), nm): 364 [\(\pi \rightarrow \pi^*\), -N = N-]; 246 [n \(\rightarrow \pi^*\), -NO\(_2\)]

\(^1H\) NMR (DMSO-d\(_6\), \(\delta\)): 0.875 - 1 [CH\(_3\) of IPDI, n, o, p]; 1.25- 2.1 [CH\(_2\) of IPDI, k, l, m]; 2.78 [CH\(_2\), exocycle of IPDI, j]; 3.1- 3.2 [1H (d), OH, g]; 3.5 [CH of IPDI, q]

4- 4.1 [1H (d), -CH-, f]; 7 [2H (m), -OCONH, h, i]; 8.5 [4H (d), phenyl, a]; 8.17 [4H (d), phenyl, b]; 8.77 [1H (s), phenyl, c]; 8.3 [1H (s), phenyl, cp]

8.2 [2H (d), phenyl, d]; 8.0 [2H (d), phenyl, e]

\(^13C\) NMR (DMSO-d\(_6\), \(\delta\)): 60 [-CHOH, (11)]; 122 (2), 124 (6,8), 126 (4), 128 (3,5,9), 130 (12-17), 133 (10), 149 (7), 152 (1) [aromatic]; 23.1- 35 [CH\(_3\) of IPDI, (27, 28, 29)]; 31.7 [-C (CH\(_3\))\(_2\) of IPDI, (24)]; 36.2 [-CH of IPDI, (22)]; 36.4 [-C- of IPDI, (26)]; 46.7- 41.4 [CH\(_2\) of IPDI, (21, 23, 25)]; 56 [CH\(_2\), exocycle of IPDI, (20)]; 156.4 [primary urethane carbonyl carbon of IPDI, (18)]; 158.2 [secondary urethane carbonyl carbon of IPDI, (19)].

5.2.2.3 Photoproduct of PU1b: Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylcyclohexane –co- cis-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2-nitro-2'-nitrosodiphenyl carbinol]: PU2b

IR (KBr, cm\(^{-1}\)): 3410 [-OH / N-H]; 2925 [-CH-]; 1710 [urethane carbonyl]; 1587 [-N = N-]; 1534, 1350 [-NO\(_2\)]; 1503 [nitroso]; 1237 [-C-O-C in –COOC- of PU]

UV (dioxane, \(\lambda_{max}\), nm): 376 [\(\pi \rightarrow \pi^*\), -N = N-]; 248 [n \(\rightarrow \pi^*\), -NO\(_2\)]
Fig. 5.2. $^1$H NMR assignments of photoproduct of PU1a [PU2a]

$^{1}$H NMR (DMSO-d$_6$, $\delta$): 0.875-1 [CH$_3$ of IPDI]; 1.25-2.1 [CH$_2$ of IPDI];
2.29 [3H (s), CH$_3$; 2.78 [CH$_2$, exocycle of IPDI]; 3.1-3.2 [1H (d), OH];
3.5 [CH of IPDI]; 4 - 4.1 [1H (d), -CH$_2$]; 7 [2H (m), -OCONH]; 8.38 [1H (d), phenyl];
8.1 [1H (d), phenyl]; 8.05 [1H (s), phenyl]; 8.47 [2H (d), phenyl]; 8.15 [2H (d), phenyl];
8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8 [2H (d), phenyl].

Fig. 5.3. $^{13}$C NMR assignments of photoproduct of PU1a [PU2a]
$^{13}$C NMR (DMSO-$d_6$, $\delta$): 20 [methyl]; 60[-CHOH]; 122, 124, 126, 127, 128, 130, 131, 133, 149, 152 [aromatic]; 23.1- 35 [CH$_3$ of IPDI]; 31.7 [-C (CH$_3$)$_2$ of IPDI];

36.2 [-CH of IPDI]; 36.4 [-C of IPDI]; 46.7- 41.4 [CH$_2$ of IPDI]; 56 [CH$_2$, exocycle of IPDI]; 156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl carbon of IPDI].

5.2.2.4 Photoproduct of PUc: Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylcyclohexane -co- cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU2c

IR (KBr, cm$^{-1}$): 3411 [-OH / N-H]; 2928 [-CH-]; 1725 [urethane carbonyl]; 1587 [-N = N-]; 1532, 1350 [-NO$_2$]; 1237 [-C-O-C in -COOC- of PU]

UV (dioxane, $\lambda$max, nm): 379 [$\pi$ $\rightarrow$ $\pi^*$, -N = N-]; 252 [$n$ $\rightarrow$ $\pi^*$, -NO$_2$]

$^1$H NMR (DMSO-$d_6$, $\delta$): 0.875- 1 [CH$_3$ of IPDI]; 1.25- 2.1 [CH$_2$ of IPDI]; 2.29 [6H (s), twoCH$_3$]; 2.78 [CH$_2$, exocycle of IPDI]; 3.1- 3.2 [1H (d), OH]; 3.5 [CHO of IPDI]; 4 - 4.1 [1H (d), -CH-]; 7 [2H (m), -OCONH]; 8.05 [2H (d), phenyl]; 8.1 [2H (d), phenyl]; 8.38 [2H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8 [2H (d), phenyl].

$^{13}$C NMR (DMSO-$d_6$, $\delta$): 20 [methyl]; 60 [-CHOH]; 122, 124, 126, 127, 128, 130, 131, 133, 149, 152 [aromatic]; 23.1- 35 [CH$_3$ of IPDI]; 31.7 [-C (CH$_3$)$_2$ of IPDI];

36.2 [-CH of IPDI]; 36.4 [-C of IPDI]; 46.7- 41.4 [CH$_2$ of IPDI] 56[CH$_2$, exocycle of IPDI]; 156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl carbon of IPDI].
5.2.2.5 Results and discussion

The orange-red colour of the solution was changed to orange-yellow on irradiation. The TLC examination of the irradiated solution after 23 h showed the complete conversion of the starting material. The IR spectra of the photoproduct of PU1a, PU1b and PU1c showed absorption bands of nitro group at ~ 1350 and ~ 1530 cm$^{-1}$ at reduced intensity and a new band appeared at ~ 1503 cm$^{-1}$ due to the formation of the nitroso group. The partial oxidation of $-\text{CH}_2$ group to $-\text{CHOH}$ at the expense of the reduction of one of the nitro groups in the molecule to nitroso group was confirmed by the shift in frequency of the NO$_2$- absorption in IR and the appearance of new peaks at $\delta$ 4 and 3.1 in the $^1$H NMR spectra and the peak at $\delta$ 60 in $^{13}$C NMR spectra. The isomerisation of the azo chromophore in the molecule was established by the shift of IR absorption at ~ 1618 cm$^{-1}$ of PU1a, PU1b and PU1c to ~ 1585 cm$^{-1}$ in PU2a, PU2b and PU2c. This was further confirmed by the shift of $\lambda_{\text{max}}$ of azo group (370 to 364; 376 to 374; 379 to 376) to shorter wavelength.

The absorption band due to polyurethane carbonyl at 1703 – 1725 cm$^{-1}$ remained unchanged, even after irradiation, indicative of the stability of the polyurethane bond in this molecule, i.e., no photodegradation took place during photolysis. Moreover, $< M >_n$ and $< M >_w$ of the photoproducts PU2a / PU2b / PU2c were ~ 11736 and ~ 23168 respectively. Thus the PDI of the photoproduct is almost the same as that of the starting material. This further confirms the absence of photodegradation during photolysis. The results indicate that the photoproducts obtained from PU1a, PU1b and PU1c are of the same type.
Mechanism

The spectral data of the photoproducts from PU1a, PU1b and PU1c confirmed that the phototransformations occurred in the polyurethanes were similar to that reported in chapter 3 for the low molecular weight bis (4-hydroxyphenylazo)-2, 2'-dinitrodiphenyl methane derivatives. Therefore, the mechanism suggested for the phototransformations in the above low molecular weight organic compound is also operative in the photolysis of the above polyurethanes. The azo group undergoes trans-cis isomerisation and one of the nitro groups in the molecule is reduced to nitroso group and the –CH₂ group is partially oxidised to –CHOH group (scheme 5.1).
Scheme 5.1 Mechanism of Phototransformation of PU1a / PU1b / PU1c

a: \( X = X' = H \);  
b: \( X = H, X' = \text{CH}_3 \);  
c: \( X = X' = \text{CH}_3 \)
5.2.2.6 Photolysis of Polyurethanes (PU1a / PU1b / PU1c) based on Isophorone diisocyanate and 2c / 2d /2e in acidified 2-propanol

A solution of the polyurethanes (PU1a / PU1b / PU1c, 500 mg) in pure dry 2-propanol (1000 mL) containing 1mL conc. H₂SO₄, was irradiated in a water-cooled photoreactor for 17 h, using a high pressure mercury vapour lamp. The UV-Vis absorption readings of the solution were recorded before and after irradiation at regular intervals of time. Typically, the results for PU1a are given in Table 5.3. The solution was then neutralised with anhydrous sodium carbonate. The solution on work-up gave the photoproducts and was identified as PU2a, PU2b, PU2c, corresponding to PU1a / PU1b / PU1c respectively, on the basis of spectral data. The spectral data of the photoproducts are given below:

Table 5.3 Variation of λ max and absorbance with UV exposure time of PU1a in acidified 2-propanol

<table>
<thead>
<tr>
<th>Time of UV exposure (in hours)</th>
<th>λ max ( nm )</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>376 ; 248</td>
<td>0.513 ; 0.430</td>
</tr>
<tr>
<td>4</td>
<td>378 ; 232</td>
<td>0.390 ; 0.298</td>
</tr>
<tr>
<td>10</td>
<td>378 ; 246</td>
<td>0.560 ; 0.438</td>
</tr>
<tr>
<td>15</td>
<td>378 ; 248</td>
<td>0.271 ; 0.265</td>
</tr>
<tr>
<td>17</td>
<td>378 ; 248</td>
<td>0.453 ; 0.421</td>
</tr>
</tbody>
</table>
5.2.2.7 Photoproduct of PU1a: Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylcyclohexane –co- cis-bis (4-hydroxyphenylazo)-2-nitro-2′-nitrosodiphenyl carbinol]: PU2a

IR (KBr, cm\(^{-1}\)): 3400 [-OH / N-H]; 2925 [-CH-]; 1703 [urethane carbonyl]; 1585 [-N = N-]; 1532, 1348 [-NO\(_2\)]; 1504 [nitroso]; 1236 [-C-O-C in –COOC- of PU]

UV (dioxane, \(\lambda_{\text{max}}\), nm): 364 [\(\pi \rightarrow \pi^*\), -N = N-]; 246 [n \(\rightarrow \pi^*\), -NO\(_2\)].

\(^1\)H NMR (DMSO-d\(_6\), \(\delta\)): 0.875- 1 [CH\(_3\) of IPDI]; 1.25- 2.1 [CH\(_2\) of IPDI]; 2.78 [CH\(_2\), exocycle of IPDI]; 3.1- 3.2 [1H (d), OH]; 3.5 [CHOH]; 4- 4.1 [1H (d), -CH-]; 7 [2H (m), -OCONH]; 8.5 [4H (d), phenyl]; 8.17 [4H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.0 [2H (d), phenyl]; 122, 124, 126, 128, 130, 133, 149 [aromatic]; 23.1- 35 [CH\(_3\) of IPDI]; 31.7 [-C (CH\(_3\))\(_2\) of IPDI]; 36.2 [-CH of IPDI]; 36.4 [-C- of IPDI]; 46.7- 41.4 [CH\(_2\) of IPDI]; 56 [CH\(_2\), exocycle of IPDI]; 156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl carbon of IPDI].

5.2.2.8 Photoproduct of PU1b: Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylcyclohexane –co- cis -4-hydroxy-3-methylphenylazo-4′-hydroxyphenylazo-2-nitro-2′-nitrosodiphenylcarbinol]: PU2b

IR (KBr, cm\(^{-1}\)): 3405 [-OH / N-H]; 2925 [-CH-]; 1710 [urethane carbonyl]; 1587 [-N = N-]; 1530, 1347 [-NO\(_2\)]; 1504 [nitroso]; 1236 [-C-O-C in –COOC- of PU]

UV (dioxane, \(\lambda_{\text{max}}\), nm): 374 [\(\pi \rightarrow \pi^*\), -N = N-]; 246 [n \(\rightarrow \pi^*\), -NO\(_2\)].

\(^1\)H NMR (DMSO-d\(_6\), \(\delta\)): 0.875- 1 [CH\(_3\) of IPDI]; 1.25- 2.1 [CH\(_2\) of IPDI]; 2.29 [3H(s), CH\(_3\)]; 2.78 [CH\(_2\), exocycle of IPDI]; 3.1- 3.2 [1H (d), OH];
3.5 \:[\text{CH of IPDI}]: \:4 - 4.1 \:[1\text{H (d), -CH-}]; \:7 \:[2\text{H (m), -OCONH}]; \:8.38 \:[1\text{H (d), phenyl}];
8.1 \:[1\text{H (d), phenyl}]; \:8.05 \:[1\text{H (s), phenyl}]; \:8.47 \:[2\text{H (d), phenyl}]; \:8.15 \:[2\text{H (d), phenyl}];
8.77 \:[1\text{H (s), phenyl}]; \:8.2 \:[2\text{H (d), phenyl}]; \:8.3 \:[1\text{H (s), phenyl}]; \:8.0 \:[2\text{H (d), phenyl}].

^{13}\text{C} \text{NMR (DMSO-d}_6, \delta): \:20 \:[\text{methyl}]; \:60 \:[-\text{CHOH}]; \:122, 124, 126, 127, 128,
130, 131, 133, 149, 152 \:[\text{aromatic}]; \:23.1 - 35 \:[\text{CH}_3 \text{ of IPDI}]; \:31.7 \:[-\text{(CH}_3)_2 \text{ of IPDI}];
36.2 \:[-\text{CH of IPDI}]; \:36.4 \:[-\text{C- of IPDI}]; \:46.7 - 41.4 \:[\text{CH}_2 \text{ of IPDI}]; \:56 \:[\text{CH}_2, \text{ exocycle of IPDI}];
156.4 \:[\text{primary urethane carbonyl carbon of IPDI}]; \:158.2 \:[\text{secondary urethane carbonyl carbon of IPDI}].

5.2.2.9 \text{Photoproduct of PU}1\text{c}: \text{Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylcyclohexane -co- cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU}2\text{c}

\text{IR (KBr, cm}^{-1}): \:3400 \:[-\text{OH / N-H}]; \:2924 \:[-\text{CH-}]; \:1725 \:[\text{urethane carbonyl}];
1587 \:[-\text{N = N-}]; \:1532, 1352 \:[-\text{NO}_2]; \:1503 \:[\text{nitroso}]; \:1236 \:[-\text{C-O-C in } -\text{COOC- of PU}].

\text{UV (dioxane, } \lambda_{\text{max}}, \text{ nm}): \:376 [\pi \rightarrow \pi^*, -\text{N = N-}]; \:250 [n \rightarrow \pi^*, -\text{NO}_2].

^{1}\text{H} \text{NMR (DMSO-d}_6, \delta): \:0.875 - 1 \:[\text{CH}_3 \text{ of IPDI}]; \:1.25 - 2.1 \:[\text{CH}_2 \text{ of IPDI}];
2.29 \:[6\text{H (s), twoCH}_3]; \:2.78 \:[\text{CH}_2, \text{ exocycle of IPDI}]; \:3.1 - 3.2 \:[1\text{H (d), OH}];
3.5 \:[\text{CH of IPDI}]; \:4 - 4.1 \:[1\text{H (d), -CH-}]; \:7 \:[2\text{H (m), -OCONH}]; \:8.05 \:[2\text{H (d), phenyl}];
8.1 \:[2\text{H (d), phenyl}]; \:8.38 \:[2\text{H (d), phenyl}]; \:8.77 \:[1\text{H (s), phenyl}]; \:8.3 \:[1\text{H (s), phenyl}];
8.2 \:[2\text{H (d), phenyl}]; \:8.0 \:[2\text{H (d), phenyl}].

^{13}\text{C} \text{NMR (DMSO-d}_6, \delta): \:20 \:[\text{methyl}]; \:60 \:[-\text{CHOH}]; \:122, 124, 126, 127, 128,
130, 131, 133, 149, 152 \:[\text{aromatic}]; \:23.1 - 35 \:[\text{CH}_3 \text{ of IPDI}]; \:31.7 \:[-\text{(CH}_3)_2 \text{ of IPDI}];
36.2 \:[-\text{CH of IPDI}]; \:36.4 \:[-\text{C- of IPDI}]; \:46.7 - 41.4 \:[\text{CH}_2 \text{ of IPDI}]; \:56 \:[\text{CH}_2, \text{ exocycle of IPDI}].
5.2.2.10 Results and discussion

The colour of the solution was changed from orange-red to orange-yellow, on irradiation. The TLC examination of the irradiated solution after 17 h showed the complete conversion of the starting material. The IR spectrum of the photoproduct of PU1a, PU1b and PU1c showed absorption bands of nitro group at \( \sim 1350 \) and \( 1530 \) cm\(^{-1}\) at reduced intensity and a new band appeared at \( \sim 1504 \) cm\(^{-1}\) due to the formation of nitroso group. The partial oxidation of -CH\(_2\) group to -CHOH at the expense of the reduction of one of the nitro groups in the molecule to nitroso group was confirmed by the shifting of frequency of \(-\text{NO}_2\) absorption in IR and the appearance of new peaks at \( \delta \) 3.1 and 4 in \(^1\text{H NMR}\) and at \( \delta \) 60 in \(^{13}\text{C NMR}\) spectrum. The isomerisation of the azo chromophore in the molecule is established by the shifting of the IR absorption at 1618 to \( \sim 1587 \) cm\(^{-1}\). This was further confirmed by the shifting of the \( \lambda_{\text{max}} \) of azo group to shorter wavelengths (370 to 364; 376 to 374 and 379 to 376 respectively).

Thus the photoproducts obtained by the photolysis of PU1a, PU1b and PU1c in acidified 2-propanol is the same as that obtained from neutral 2-propanol. However, in acidified 2-propanol, the photoreaction takes place at a faster rate than that in neutral 2-propanol.

5.2.2.11 Photolysis of Polyurethanes (PU1a / PU1b / PU1c) based on Isophorone diisocyanate and 2c / 2d / 2e in neutral ethyl acetate

The polyurethane (PU1a / PU1b / PU1c, 500 mg) was dissolved in 1000 mL of pure dry ethyl acetate. The solution was irradiated for 20 h and was worked up as before.
Typically, the results for PU1a are given in Table 5.4. The residue photoproduct was identified as PU2a / PU2b / PU2c, corresponding to PU1a / PU1b / PU1c respectively, on the basis of spectral data. The spectral data of the photoproducts are given below:

5.2.2.12 Photoproduct of PU1a: Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylocyclohexane –co- cis-bis (4-hydroxyphenylazo)-2-nitro-2'-nitrosodiphenyl carbinol]: PU2a

IR (KBr, cm\(^{-1}\)): 3410 [-OH / N-H]; 2923 [-CH-]; 1704 [urethane carbonyl]; 1587 [-N = N-]; 1532, 1351 [-NO\(_2\)]; 1504 [-C-O-C in –COOC- of PU]

UV (dioxane, \(\lambda_{max}\), nm): 364 [\(\pi \rightarrow \pi^*\), -N = N-]; 248 [\(\pi \rightarrow \pi^*\), -NO\(_2\)].

\(^1\)H NMR (DMSO-d\(_6\), \(\delta\)): 0.87-1.0 [CH\(_3\) of IPDI]; 1.25-2.1 [CH\(_2\) of IPDI]; 2.78 [CH\(_2\), exocycle of IPDI]; 3.1-3.2 [1H (d), OH]; 3.5 [CH of IPDI]; 4.4-4.1 [1H (d), -CH-]; 7 [2H (m), -OCONH]; 8.5 [4H (d), phenyl]; 8.17 [4H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.0 [2H (d), phenyl].

\(^13\)C NMR (DMSO-d\(_6\), \(\delta\)): 60 [-CHOH]; 122, 124, 126, 128, 130, 133, 149, 152 [aromatic]; 23.1-35 [CH\(_3\) of IPDI]; 31.7[-C (CH\(_3\))\(_2\) of IPDI]; 36.2 [-CH of IPDI]; 36.4 [-C- of IPDI]; 46.7-41.4 [CH\(_2\) of IPDI]; 56 [CH\(_2\), exocycle of IPDI]; 156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl carbon of IPDI].

5.2.2.13 Photoproduct of PU1b: Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylcyclohexane –co- cis-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2-nitro-2'-nitrosodiphenylcarbinol]: PU2b

IR (KBr, cm\(^{-1}\)): 3411 [-OH / N-H]; 2925 [-CH-]; 1710 [urethane carbonyl]; 1585 [-N = N-]; 1530, 1351 [-NO\(_2\)]; 1504 [nitroso]; 1237 [-C-O-C in –COOC- of PU]
UV (dioxane, $\lambda_{\text{max}}$, nm): 374 [$\pi \rightarrow \pi^*$, $-\text{N} = \text{N}$-]; 248 [$n \rightarrow \pi^*$, $-\text{NO}_2$]

$^1$H NMR (DMSO-$_d_6$, $\delta$): 0.875-1 [CH$_3$ of IPDI]; 1.25-2.1 [CH$_2$ of IPDI];
2.29 [3H (s), CH$_3$]; 2.78 [CH$_2$, exocycle of IPDI]; 3.1-3.2 [1H (d), OH];
3.5 [CH of IPDI]; 4 - 4.1 [1H (d), -CH$_2$-]; 7 [2H (m), -OCONH]; 8.38 [1H (d), phenyl]; 8.1 [1H (d), phenyl]; 8.05 [1H (s), phenyl]; 8.47 [2H (d), phenyl]; 8.15 [2H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8 [2H (d), phenyl].

$^{13}$C NMR (DMSO-$_d_6$, ppm): 20 [methyl]; 60 [-CHOH]; 122, 124, 126, 127, 128, 130, 131, 133, 149, 152 [aromatic]; 23.1-35 [CH$_3$ of IPDI]; 31.7 [-C (CH$_3$)$_2$ of IPDI]; 36.2 [-CH of IPDI]; 36.4 [-C- of IPDI]; 46.7-41.4 [CH$_2$ of IPDI]; 56 [CH$_2$, exocycle of IPDI]; 156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl carbon of IPDI].

5.2.2.14 Photoproduct of PU$^c_1$: Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylcyclohexane –co- cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU$^c_2$

IR (KBr, cm$^{-1}$): 3411 [-OH / N-H]; 2925 [-CH$_2$-]; 1725 [urethane carbonyl];
1587 [-N = N-]; 1530, 1531 [-NO$_2$]; 1503 [nitroso]; 1237 [-C-O-C in –COOC- of PU]

UV (dioxane, $\lambda_{\text{max}}$, nm): 376 [$\pi \rightarrow \pi^*$, $-\text{N} = \text{N}$-]; 252 [$n \rightarrow \pi^*$, $-\text{NO}_2$];

$^1$H NMR (DMSO-$_d_6$, $\delta$): 0.875-1 [CH$_3$ of IPDI]; 1.25-2.1 [CH$_2$ of IPDI];
2.29 [6H (s), twoCH$_3$]; 2.78 [CH$_2$, exocycle of IPDI]; 3.1-3.2 [1H (d), OH];
3.5 [CH of IPDI]; 4 - 4.1 [1H (d), -CH$_2$-]; 7 [2H (m), -OCONH]; 8.05 [2H (d), phenyl];
8.1 [2H (d), phenyl]; 8.38 [2H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.0 [2H (d), phenyl].
$^{13}$C NMR (DMSO-d$_6$, δ): 20 [methyl]; 60[-CHOH]; 122, 124, 126, 127, 128, 130, 131, 133, 149, 152 [aromatic]; 23.1 - 35 [CH$_3$ of IPDI]; 31.7 [-C (CH$_3$)$_2$ of IPDI]; 36.2 [-CH of IPDI]; 36.4 [-C- of IPDI]; 46.7 - 41.4 [CH$_2$ of IPDI]; 56 [CH$_2$, exocycle of IPDI]; 156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl carbon of IPDI].

Table 5.4 Variation of λ$_{\text{max}}$ and absorbance with UV irradiation time of PU1a in neutral ethyl acetate

<table>
<thead>
<tr>
<th>Time of UV exposure (in hrs)</th>
<th>λ$_{\text{max}}$ (nm)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>372.5</td>
<td>0.198</td>
</tr>
<tr>
<td>4</td>
<td>371.5 ; 255</td>
<td>0.481 ; 0.448</td>
</tr>
<tr>
<td>10</td>
<td>370 ; 250.5</td>
<td>0.269 ; 0.277</td>
</tr>
<tr>
<td>15</td>
<td>370 ; -----</td>
<td>0.223 ; -----</td>
</tr>
<tr>
<td>20</td>
<td>372.5 ; 252.5</td>
<td>0.275 ; 0.185</td>
</tr>
</tbody>
</table>

5.2.2.15 Results and discussion

Almost all of the spectral observations are similar to that for the photolysis of PU1a / PU1b / PU1c in neutral 2-propanol. Therefore, the photoproducts are identified as PU2a / PU2b / PU2c respectively.

5.2.2.16 Photolysis of Polyurethanes (PU1a / PU1b / PU1c) based on Isophorone diisocyanate and 2c / 2d / 2e in acidified ethyl acetate

The polyurethane (PU1a / PU1b / PU1c, 500 mg) was dissolved in 1000 mL of pure dry ethyl acetate containing 1mL of conc. H$_2$SO$_4$. The solution was irradiated for 15 h and
the experiment was done similar to the photolysis in acidified 2-propanol. The photoproduct was identified as PU2a / PU2b / PU2c, corresponding to PU1a / PU1b / PU1c respectively, on the basis of spectral data:

5.2.2.17 Photoproduct of PU1a: Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylcyclohexane \(-co-\) cis-bis (4-hydroxyphenylazo)-2-nitro-2'-nitrosodiphenyl carbinol]: PU2a

IR (KBr, cm\(^{-1}\)): 3399 [-OH / N-H]; 2923 [-CH-]; 1704 [urethane carbonyl]; 1601 [-N = N-]; 1530, 1347 [-NO\(_2\)]; 1504 [-C-O-C in -COOC- of PU].

UV (dioxane, \(\lambda_{\text{max}}\), nm): 364.5 [\(\pi \rightarrow \pi^*\), -N = N-]; 248 [n \rightarrow \pi^*, -NO\(_2\)].

\(^1\)H NMR (DMSO-d\(_6\), \(\delta\)): 0.875-1 [CH\(_3\) of IPDI]; 1.25-2.1 [CH\(_2\) of IPDI]; 2.78 [CH\(_2\), exocycle of IPDI]; 3.1-3.2 [1H (d), OH]; 3.5 [CH of IPDI]; 4-4.1 [1H (d), -CH-]; 7 [2H (m), -OCONH]; 8.5 [4H (d), phenyl]; 8.17 [4H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.20 [2H (d), phenyl]; 8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl].

\(^{13}\)C NMR (DMSO-d\(_6\), \(\delta\)): 60 [-CHOH]; 122, 124, 126, 128, 130, 133, 149, 152 [aromatic]; 23.1-35 [CH\(_3\) of IPDI]; 31.7 [-C(CH\(_3\))\(_2\) of IPDI]; 36.2 [CH of IPDI]; 36.4 [-C of IPDI]; 46.7-41.4 [CH\(_2\) of IPDI]; 56 [CH\(_2\), exocycle of IPDI]; 156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl carbon of IPDI].

5.2.2.18 Photoproduct of PU1b: Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylcyclohexane \(-co-\) cis-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2-nitro-2'-nitrosodiphenylcarbinol]: PU2b

IR (KBr, cm\(^{-1}\)): 3412 [-OH / N-H]; 2923 [-CH-]; 1710 [urethane carbonyl]; 1590 [-N = N-]; 1531, 1347 [-NO\(_2\)]; 1503 [nitroso]; 1236 [-C-O-C in -COOC- of PU]

UV (dioxane, \(\lambda_{\text{max}}\), nm): 374 [\(\pi \rightarrow \pi^*\), -N = N-]; 245 [n \rightarrow \pi^*, -NO\(_2\)]
\(^{1}\text{H NMR (DMSO-d}_6, \delta):\) 0.875- 1 [CH\(_3\) of IPDI]; 1.25- 2.1 [CH\(_2\) of IPDI];

2.29 [3H(s), CH\(_3\)]; 2.78 [CH\(_2\), exocycle of IPDI]; 3.1- 3.2 [1H (d), OH]; 3.5 [CH of

IPDI]; 4 - 4.1 [1H (d), -CH-]; 7 [2H (m), -OCONH]; 8.38 [1H (d), phenyl]; 8.1 [1H (d),

phenyl]; 8.05 [1H (s), phenyl]; 8.47 [2H (d), phenyl]; 8.15 [2H (d), phenyl]; 8.77 [1H (s),

phenyl]; 8.2 [2H (d), phenyl]; 8.3 [1H (s), phenyl]; 8 [2H (d), phenyl].

\(^{13}\text{C NMR (DMSO-d}_6, \delta):\) 20 [methyl]; 60[-CHOH]; 122, 124, 126, 127, 128, 130, 131,

133, 149, 152 [aromatic]; 23.1- 35 [CH\(_3\) of IPDI]; 31.7 [-C (CH\(_3\))\(_2\) of IPDI]; 36.2 [-CH of

IPDI]; 36.4 [-C of IPDI]; 46.7- 41.4 [CH\(_2\) of IPDI]; 56[CH\(_2\), exocycle of IPDI];

156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl

carbon of IPDI].

5.2.2.19 Photoproduct of PU1c: Poly [5-isocyanato-1-(isocyanatomethyl)-1, 3, 3-

trimethylcyclohexane –co- cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2’-
nitrosodiphenylcarbinol]: PU2c

IR (KBr, cm\(^{-1}\)): 3411 [-OH / N-H]; 2923 [-CH-]; 1725 [urethane carbonyl];

1590 [-N = N-]; 1531, 1347 [-NO\(_2\)]; 1504 [nitroso]; 1238 [-C-O-C in –COOC- of PU].

UV (dioxane, \(\lambda_{\text{max}}, \text{nm})): 376 [\(\pi \rightarrow \pi^*\), -N = N-]; 250 [\(\pi \rightarrow \pi^*\), -NO\(_2\)].

\(^{1}\text{H NMR (DMSO-d}_6, \delta):\) 0.875- 1 [CH\(_3\) of IPDI]; 1.25- 2.1 [CH\(_2\) of IPDI];

2.29 [6H (s), twoCH\(_3\)]; 2.78 [CH\(_2\), exocycle of IPDI]; 3.1- 3.2 [1H (d), OH];

3.5 [CH of IPDI]; 4 - 4.1 [1H (d), -CH-]; 7 [2H (m), -OCONH]; 8.05 [2H (d), phenyl];

8.1 [2H (d), phenyl]; 8.38 [2H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl];

8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl].

\(^{13}\text{C NMR (DMSO-d}_6, \delta):\) 20 [methyl]; 60 [-CHOH]; 122, 124, 126, 127, 128, 130, 131,

133, 149, 152 [aromatic]; 23.1- 35 [CH\(_3\) of IPDI]; 31.7 [-C (CH\(_3\))\(_2\) of IPDI]; 36.2 [-CH of
IPDI]; 36.4 [-C- of IPDI]; 46.7- 41.4 [CH₂ of IPDI]; 56 [CH₂, exocycle of IPDI]; 156.4 [primary urethane carbonyl carbon of IPDI]; 158.2 [secondary urethane carbonyl carbon of IPDI].

### 5.2.2.20 Results and discussion

The spectral observations are similar to that for the photolysis of PU1a / PU1b / PU1c in acidified 2-propanol. Therefore, the photoproducts are identified as PU2a / PU2b / PU2c respectively.

The irradiation of polyurethanes containing o-nitrobenzyl chromophore leads to photoreduction products through hydrogen abstraction from the methylene group by the lowest excited triplet state of the nitro group in the compound. In the presence of the azo groups, only one of the electronically excited nitro groups in the molecule is partially reduced to a nitroso function while an oxygen atom is inserted into the C-H bond of the methylene group at the ortho position. Protic solvents and acidified solvents are found to catalyse and speed up the redox reaction.

Thus, the polyurethanes containing azo and nitro groups can be photorestructured without degradation and their photostability under UV-light was found to be significant over a long duration of time.

### 5.2.3 Photolysis of Polyurethanes based on HMDI

#### 5.2.3.1 Photolysis of Polyurethanes (PU3a / PU3b / PU3c) based on Hexamethylene diisocyanate and 2c / 2d / 2e in neutral 2-propanol

The polyurethane (PU3a / PU3b / PU3c, 500 mg) was dissolved in 1000 mL of pure dry 2-propanol. The solution was irradiated for 26 h and was worked up as before. The
residue photoproduct was identified as PU4a / PU4b / PU4c corresponding to PU3a / PU3b / PU3c respectively on the basis of spectral data:

5.2.3.2 Photoproduct of PU3a: Poly [1, 6-diisocyanatohexane -co- cis-bis (4-hydroxyphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU4a

IR (KBr, cm⁻¹): 3323 [-OH / N-H]; 2923 [-CH-]; 1689 [urethane carbonyl]; 1581 [-N = N-]; 1531, 1348 [-N02]; 1504 [nitroso]; 1234 [-C-O-C in -COOC- of PU].

UV (dioxane, λmax, nm): 368 [π → π * , -N = N-]; 248 (π → π * , -N02).

¹H NMR (DMSO-d₆, δ): 1.18-2.75 [H of HMDI, I, k, j]; 3.1-3.2 [1H (d), OH, h]; 4-4.1 [1H (d), -CH-, g]; 6.9 [2H (m), -OCONH, i]; 8.5 [4H (d), phenyl, a]; 8.17 [4H (d), phenyl, b]; 8.77 [1H (s), phenyl, c]; 8.2 [2H (d), phenyl, d]; 8.3 [1H (s), phenyl, f]; 8.0 [2H (d), phenyl, e].

¹³C NMR (DMSO-d₆, δ): 60 [-CHOH, (11)]; 122 (2), 124 (6, 8), 126 (4), 128 (35, 9), 130 (12-17), 133 (10), 149 (7), 152 (1) [aromatic]; 26.01-40.12 [-CH₂ of HDI, (21, 20, 19)]; 157.7 [-OCONH, (18)].

Fig.5.4. ¹H NMR assignments of photoproduct of PU3a [PU4a]
5.2.3.3 Photoproduct of PU3b: Poly [1, 6-diisocyanatohexane -co- cis-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2-nitro-2'-nitrosodiphenylcarbinol]: PU4b

IR (KBr, cm⁻¹): 3353 [-OH / N-H]; 2932 [-CH-]; 1720 [urethane carbonyl]; 1587 [-N = N-]; 1531, 1349 [-NO₂]; 1504 [nitroso]; 1237 [-C-O-C in -COOC- of PU].

UV (dioxane, λmax, nm): 371 [π → π⁺, -N = N-]; 252 [n → π⁺, -NO₂].

1H NMR (DMSO-d₆, δ): 1.18- 2.75 [H of HMDI]; 2.29 [3H (s), CH₃]; 3.1-3.2 [1H (d), OH]; 4 - 4.1 [1H (d), -CH-]; 6.9 [2H (m), -OCONH]; 8.38 [1H (d), phenyl]; 8.1 [1H (d), phenyl]; 8.05 [1H (s), phenyl]; 8.47 [2H (d), phenyl]; 8.15 [2H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl].

13C NMR (DMSO-d₆, δ): 20 [methyl]; 60 [-CHOH]; 122, 124, 126, 127, 128, 130, 131, 133, 149, 152 [aromatic]; 26.01 - 40.12 [-CH₂ of HDI]; 157.7 [-OCONH].
5.2.3.4 Photoproduct of PU3c: Poly [1, 6-diisocyanatohexane -co- cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU4c

IR (KBr, cm\(^{-1}\)): 3370 [-OH / N-H]; 2924 [-CH-]; 1723 [urethane carbonyl];
1595 [-N = N-]; 1532, 1352 [-NO\(_2\)]; 1503 [nitroso]; 1244 [-C-O-C in -COOC- of PU].

UV (dioxane, \(\lambda_{max}\), nm): 374 [\(\pi \rightarrow \pi^*\), -N = N-]; 250 [\(n \rightarrow \pi^*\), -NO\(_2\)].

\(^1\)H NMR (DMSO-d\(_6\), \(\delta\)): 1.18- 2.75 [H of HMDI]; 2.29 [6H (s), twoCH\(_3\)];
3.1- 3.2 [1H (d), OH]; 4 - 4.1 [1H (d), -CH-]; 6.9 [2H (m), -OCONH];
8.05 [2H (d), phenyl]; 8.1 [2H (d), phenyl]; 8.38 [2H (d), phenyl];
8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.0 [2H (d), phenyl].

\(^13\)C NMR (DMSO-d\(_6\), \(\delta\)): 20 [methyl]; 60 [-CHOH]; 122, 124, 126, 127, 128, 130, 131, 133, 149, 152 [aromatic]; 26.01- 40.12 [-CH\(_2\) of HDI]; 157.7 [-OCONH].

5.2.3.5 Results and discussion

The IR, UV and NMR (\(^1\)H and \(^13\)C) of the photoproduct of PU3a / PU3b / PU3c reveal that the photoreactions taking place are similar to the photoreactions of PU1a / PU1b / PU1c. Therefore, the photoproducts of PU3a / PU3b / PU3c are identified as PU4a / PU4b / PU4c respectively. However, it is found that compared to the photoreactions of polyurethanes based on IPDI, the photoreactions of polyurethanes based on HMDI, took place at a lower rate.

5.2.3.6 Photolysis of Polyurethanes (PU3a / PU3b / PU3c) based on Hexamethylene diisocyanate and 2c / 2d / 2e in acidified 2-propanol

The polyurethane (PU3a / PU3b / PU3c, 500 mg) was dissolved in 1000 mL of pure dry 2-propanol, containing 1mL of conc. H\(_2\)SO\(_4\). The solution was then irradiated for 15 h and was then worked up as in the case of PU1a / PU1b / PU1c in acidified 2-propanol.
The residue photoproduct was identified as PU4a / PU4b / PU4c, corresponding to PU3a / PU3b / PU3c respectively on the basis of spectral data:

5.2.3.7 Photoproduct of PU3a: Poly [1, 6-diisocyanatohexane -co- cis-bis (4-hydroxyphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU4a

IR (KBr, cm\(^{-1}\)): 3407 [-OH / N-H]; 2923 [-CH-]; 1689 [urethane carbonyl];
1580 [-N = N-]; 1531, 1349 [-NO\(_2\)]; 1503 [nitroso]; 1241 [-C-O-C in -COOC- of PU].

UV (dioxane, \(\lambda_{\text{max}}, \text{nm}\)): 369 [\(\pi \rightarrow \pi^*\), -N = N-]; 248 [n \(\rightarrow \pi^*\), -NO\(_2\)].

\(^1\)H NMR (DMSO-\(d_6\), \(\delta\)): 1.18- 2.75 [H of HMDI]; 3.1- 3.2 [1H (d), OH]; 4- 4.1 [1H (d), -CH-]; 6.9 [2H (m), -OCONH]; 8.5 [4H (d), phenyl]; 8.17 [4H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.0 [2H (d), phenyl].

\(^{13}\)C NMR (DMSO-\(d_6\), \(\delta\)): 60 [-CHOH]; 122, 124, 126, 128, 130, 133, 149, 152 [aromatic]; 26.01- 40.12 [-CH\(_2\) of HDI]; 157.7 [-OCONH].

5.2.3.8 Photoproduct of PU3b: Poly [1, 6-diisocyanatohexane -co- cis-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2-nitro-2'-nitrosodiphenylcarbinol]: PU4b

IR (KBr, cm\(^{-1}\)): 3380 (-OH / N-H); 2932 (-CH-); 1720 (urethane carbonyl);
1587 [-N = N-]; 1531, 1349 (-NO\(_2\)); 1504 (nitroso); 1241 (-C-O-C in -COOC- of PU).

UV (dioxane, \(\lambda_{\text{max}}, \text{nm}\)): 372 (\(\pi \rightarrow \pi^*\), -N = N-); 250 [n \(\rightarrow \pi^*\), -NO\(_2\)].

\(^1\)H NMR (DMSO-\(d_6\), \(\delta\)): 1.18- 2.75 [H of HMDI]; 2.29 [3H (s), CH\(_3\)]; 3.1- 3.2 [1H (d), OH]; 4 - 4.1 [1H (d), -CH-]; 6.9 [2H (m), -OCONH]; 8.38 [1H (d), phenyl]; 8.1 [1H (d), phenyl]; 8.05 [1H (s), phenyl]; 8.47 [2H (d), phenyl]; 8.15 [2H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl].
\(^{13}\)C NMR (DMSO-d\(_6\), \(\delta\)): 20 [methyl]; 60 [-CHOH]; 122, 124, 126, 127, 128, 130, 131, 133, 149, 152 [aromatic]; 26.01-40.12 [-CH\(_2\) of HDI]; 157.7 [-OCONH].

5.2.3.9 Photoproduct of PU3c: Poly [1, 6-diisocyanatohexane -co- cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU4c

IR (KBr, cm\(^{-1}\)): 3400 [-OH / N-H]; 2924 [-CH\(_2\)]; 1723 [urethane carbonyl]; 1595[-N = N-]; 1532, 1532 [-NO\(_2\)]; 1503 [nitroso]; 1244 [-C-O-C in -COOC- of PU].

UV (dioxane, \(\lambda_{\text{max}}\), nm): 374 [$\pi \rightarrow \pi^*$, -N = N-]; 250 [n \rightarrow \pi^*$, -NO\(_2\)].

\(^1\)H NMR (DMSO-d\(_6\), \(\delta\)): 1.18-2.75 [H of HMDI]; 2.29 [6H (s), twoCH\(_3\)]; 3.1-3.2 [1H (d), OH]; 4-4.1 [1H (d), -CH\(_2\)-]; 6.9 [2H (m), -OCONH]; 8.05 [2H (d), phenyl]; 8.1 [2H (d), phenyl]; 8.38 [2H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.0 [2H (d), phenyl].

\(^{13}\)C NMR (DMSO-d\(_6\), \(\delta\)): 20 [methyl]; 60 [-CHOH]; 122, 124, 126, 127, 128, 130, 131, 133, 149, 152 [aromatic]; 26.01-40.12 [-CH\(_2\) of HDI]; 157.7 [-OCONH].

5.2.3.10 Results and discussion

From the IR, UV-Vis, \(^1\)H NMR and \(^{13}\)C NMR spectra of the photoproducts of PU3a / PU3b / PU3c, it is revealed that the photoreactions are similar to that taking place in PU1a / PU1b / PU1c in neutral 2-propanol. Therefore, the photoproduct of PU3a / PU3b / PU3c is identified as PU4a / PU4b / PU4c respectively (scheme 5.2). However, in acidified 2-propanol the photoreactions took place at a faster rate than that in neutral 2-propanol, because, hydrogen abstraction is more easy in acidic medium. The \(< M >_n\) and \(< M >_w\) of the photoproducts were \(~ 11244\) and \(~ 22082\) respectively. Thus the PDI of the photoproduct is almost the same as that of the starting material. This confirms the
absence of photodegradation during photolysis. The results indicate that the photoproducts obtained from PU3a, PU3b and PU3c are of similar type.

**Mechanism**

The spectral data of the photoproducts of PU3a / PU3b / PU3c suggest that the mechanism for the phototransformations during the photolysis of the polyurethanes is similar to that reported in this thesis for the low molecular weight bis (4-hydroxyphenylazo)-2, 2'-dinitrodiphenylmethane derivatives: The azo group undergoes trans-cis isomerisation, followed by an n → π * triplet excited state of the nitro group. The electronically excited nitro group abstracts a hydrogen from the nearby methylene group, forming a diradical intermediate and is then converted into the corresponding nitronic acid (aci form). The nitronic acid then cyclises to benzisoxazoline intermediate. Finally, this intermediate rearranges to nitrosocarbinol derivative of the polyurethane (scheme 5.2).
5.2.3.11 Photolysis of Polyurethanes (PU3a / PU3b / PU3c) based on Hexamethylene diisocyanate and 2c / 2d / 2e in neutral ethyl acetate

The polyurethane (PU3a / PU3b / PU3c, 500 mg) was dissolved in 1000 mL of pure dry ethyl acetate. The solution was irradiated for 15 h and was worked up as before. The residue photoproducts were identified as PU4a / PU4b / PU4c corresponding to PU3a / PU3b / PU3c respectively, on the basis of spectral data:

5.2.3.12 Photoproduct of PU3a: Poly [1, 6-diisocyanatohexane -co- cis-bis (4-hydroxyphenylazo)-2-nitro-2′-nitrosodiphenylcarbinol]: PU4a

IR (KBr, cm⁻¹): 3327 [-OH / N-H]; 2932 [-CH-]; 1689 [urethane carbonyl]; 1580 [-N = N-]; 1531, 1349 [-NO₂]; 1503 [nitroso]; 1237 [-C-O-C in -COOC- of PU].

UV (dioxane, λmax, nm): 369 [π → π⁺, -N = N-]; 249 [n → π⁺, -NO₂].

¹H NMR (DMSO-d₆, δ): 1.18- 2.75 [H of HMDI]; 3.1- 3.2 [1H (d), OH]; 4.1-4.1 [1H (d), -CH-]; 6.9 [2H (m), -OCONH]; 8.5 [4H (d), phenyl];
8.17 [4H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl].

$^{13}$C NMR (DMSO-d$_6$, $\delta$): 60 [-CHOH]; 122, 124, 126, 128, 130, 133, 149, 152 [aromatic]; 26.01 - 40.12 [-CH$_2$ of HDI]; 157.7 [-OCONH].

5.2.3.13 Photoproduct of PU3b: Poly [1, 6-diisocyanatoheaxane -co- cis-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2-nitro-2'-nitrosodiphenylcarbinol]: PU4b

IR (KBr, cm$^{-1}$): 3327 [-OH / N-H]; 2924 [-CH-]; 1720 [urethane carbonyl]; 1587 [-N = N-]; 1530, 1350 [-NO$_2$]; 1504 [-C-O-C in -COOC- of PU].

UV (dioxane, $\lambda_{max}$, nm): 370 [n $\rightarrow$ $\pi^*$, -N = N-]; 250 [n $\rightarrow$ $\pi^*$, -NO$_2$].

$^1$H NMR (DMSO-d$_6$, $\delta$): 1.18 - 2.75 [H of HMDI]; 2.29 [3H (s), CH$_3$]; 3.1 - 3.2 [1H (d), OH]; 4 - 4.1 [1H (d), -CH-]; 6.9 [2H (m), -OCONH]; 8.38 [1H (d), phenyl]; 8.1 [1H (d), phenyl]; 8.05 [1H (s), phenyl]; 8.47 [2H (d), phenyl]; 8.15 [2H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl].

$^{13}$C NMR (DMSO-d$_6$, $\delta$): 20 [methyl]; 60 [-CHOH]; 122, 124, 126, 127, 128, 130, 131, 133, 149, 152 [aromatic]; 26.01 - 40.12 [-CH$_2$ of HDI]; 157.7 [-OCONH].

5.2.3.14 Photoproduct of PU3c: Poly [1, 6-diisocyanatoheaxane -co- cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU4c

IR (KBr, cm$^{-1}$): 3400 [-OH / N-H]; 2924 [-CH-]; 1723 [urethane carbonyl]; 1588 [-N = N-]; 1530, 1351 [-NO$_2$]; 1504 [nitroso]; 1238 [-C-O-C in -COOC- of PU].

UV (dioxane, $\lambda_{max}$, nm): 374 [n $\rightarrow$ $\pi^*$, -N = N-]; 250 [n $\rightarrow$ $\pi^*$, -NO$_2$].

$^1$H NMR (DMSO-d$_6$, $\delta$): 1.18 - 2.75 [H of HMDI]; 2.29 [6H (s), twoCH$_3$]; 3.1 - 3.2 [1H (d), OH]; 4 - 4.1 [1H (d), -CH-]; 6.9 [2H (m), -OCONH];
8.05 [2H (d), phenyl]; 8.1 [2H (d), phenyl]; 8.38 [2H (d), phenyl]; 8.77 [1H (s), phenyl];
8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.0 [2H (d), phenyl].

$^{13}$C NMR (DMSO-d$_6$, δ): 20 [methyl]; 60 [-CHOH]; 122, 124, 126, 127, 128, 130, 131,
133, 149, 152 [aromatic]; 26.01- 40.12 [-CH$_2$ of HDI]; 157.7 [-OCONH].

5.2.3.15 Results and discussion
The IR, UV-Vis and NMR ($^1$H and $^{13}$C) spectra of the photoproducts of PU3a / PU3b / PU3c, revealed that the photoreactions were similar to that as before. However, the reaction in ethyl acetate was faster than that in 2-propanol. The photoproducts of PU3a / PU3b / PU3c were identified as PU4a / PU4b / PU4c respectively.

The irradiation of the polyurethanes containing o-nitrobenzyl chromophores has lead to photoreduction products through hydrogen abstraction from the methylene group by the lowest excited triplet state of the nitro group in the compound. In the presence of the azo groups, only one of the electronically excited nitro groups in the molecule was partially reduced to a nitroso function while an oxygen atom was inserted into the C-H bond of the methylene group at the ortho position. Protic solvents and acidified solvents were found to facilitate and speed up the redox reaction.

5.2.3.16 Photolysis of Polyurethanes (PU3a / PU3b / PU3c) based on Hexamethylene diisocyanate and 2c / 2d / 2e in acidified ethyl acetate
The polyurethane (PU3a / PU3b / PU3c, 500 mg) was dissolved in 1000 mL of pure dry ethyl acetate acidified with 1 mL of conc. H$_2$SO$_4$. The solution was irradiated for 12 h and was worked up as with acidified 2-propanol. The residual photoproducts were identified as PU4a / PU4b / PU4c corresponding to PU3a / PU3b / PU3c respectively on the basis of spectral data:
5.2.3.17 Photoproduct of PU3a: Poly [1, 6-diisocyanatohexane -co- cis-bis (4-hydroxyphenylazo)-2-nitro-2′-nitrosodiphenylcarbinol]: PU4a

IR (KBr, cm⁻¹): 3330 [-OH / N-H]; 2929 [-CH-]; 1689 [urethane carbonyl]; 1573 [-N = N-]; 1530, 1346 [-NO₂]; 1503 [nitroso]; 1251 [-C-O-C in -COOC- of PU]

UV (dioxane, λmax, nm): 369 [π → π⁺, -N = N-]; 250 [n → π⁺, -NO₂].

¹H NMR (DMSO-d₆, δ): 1.18- 2.75 [H of HMDI]; 3.1- 3.2 [1H (d), OH]; 4- 4.1 [1H (d), -CH-]; 6.9 [2H (m), -OCONH]; 8.5 [4H (d), phenyl]; 8.17 [4H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl].

¹³C NMR (DMSO-d₆, δ): 60 [-CHOH]; 122, 124, 126, 128, 130, 133, 149, 152 [aromatic]; 26.01- 40.12 [-CH₂ of HDI]; 157.7 [-OCONH].

5.2.3.18 Photoproduct of PU3b: Poly [1, 6-diisocyanatohexane -co- cis-4-hydroxy-3-methylphenylazo-4′-hydroxyphenylazo-2-nitro-2′-nitrosodiphenylcarbinol]: PU4b

IR (KBr, cm⁻¹): 3353 [-OH / N-H]; 2932 [-CH-]; 1720 [urethane carbonyl]; 1587 [-N = N-]; 1531, 1349 [-NO₂]; 1503 [nitroso]; 1238 [-C-O-C in -COOC- of PU].

UV (dioxane, λmax, nm): 371 [π → π⁺, -N = N-]; 250 [n → π⁺, -NO₂].

¹H NMR (DMSO-d₆, δ): 1.18- 2.75 [H of HMDI]; 2.29 [3H (s), CH₃]; 3.1- 3.2 [1H (d), OH]; 4- 4.1 [1H (d), -CH-]; 6.9 [2H (m), -OCONH]; 8.38 [1H (d), phenyl]; 8.1 [1H (d), phenyl]; 8.05 [1H (s), phenyl]; 8.47 [2H (d), phenyl]; 8.15 [2H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl].

¹³C NMR (DMSO-d₆, δ): 20 [methyl]; 60 [-CHOH]; 122, 124, 126, 127, 128, 130, 131, 133, 149, 152 [aromatic]; 26.01- 40.12 [-CH₂ of HDI]; 157.7 [-OCONH].
5.2.3.19 Photoproduct of PU3c: Poly [1, 6-diisocyanatohexane -co- cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU4c

IR (KBr, cm⁻¹): 3360 [-OH / N-H]; 2924 [-CH-]; 1723 [urethane carbonyl]; 1595 [-N = N-]; 1532, 1352 [-NO₂]; 1503 [nitroso]; 1244 [-C-O-C in -COOC- of PU].

UV (dioxane, λmax, nm): 375 [π → π⁺, -N = N-]; 250 [n → π⁺, -NO₂].

¹H NMR (DMSO-d₆, δ): 1.18- 2.75 [H of HMDI]; 2.29 [6H (s), twoCH₃]; 3.1- 3.2 [1H (d), OH]; 4 - 4.1 [1H (d), -CH-]; 6.9 [2H (m), -OCONH]; 8.05 [2H (d), phenyl]; 8.1 [2H (d), phenyl]; 8.38 [2H (d), phenyl]; 8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.0 [2H (d), phenyl].

¹³C NMR (DMSO-d₆, δ): 20 [methyl]; 60 [-CHOH]; 122, 124, 126, 127, 128, 130, 131, 133, 149, 152 [aromatic]; 26.01- 40.12 [-CH₂ of HDI]; 157.7 [-OCONH].

5.2.3.20 Results and discussion

The IR, UV and NMR (¹H and ¹³C) spectra of the photoproducts of PU3a / PU3b / PU3c reveal that the photoproducts are similar to that as before. However, the reaction in acidified ethyl acetate is faster than that in neutral ethyl acetate. The photoproduct of PU3a / PU3b / PU3c is identified as PU4a / PU4b / PU4c respectively.

5.2.4 Photolysis of Polyurethanes based on 2, 4-TDI

5.2.4.1 Photolysis of Polyurethanes (PU5a / PU5b / PU5c) of 2, 4-Toluene diisocyanate and 2c / 2d / 2e in neutral 2-propanol

The polyurethane (PU5a / PU5b / PU5c, 500 mg) was dissolved in 1000 mL of pure dry 2-propanol. The solution was irradiated for 18h and was worked up as before. The residue photoproducts were identified as PU6a / PU6b / PU6c corresponding to PU5a / PU5b / PU5c respectively on the basis of spectral data:
5.2.4.2 Photoproduct of PU5a: Poly [1-imido-4-isocyanato-2-methylbenzene-co-cis-bis (4-hydroxyphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU6a

IR (KBr, cm⁻¹): 3398 [-OH / N-H]; 2923 [-CH-]; 1680 [imide carbonyl]; 1599 [-N = N-]; 1530, 1346 [-NO₂]; 1504 [nitroso].

UV (dioxane, λmax, nm): 369 (π → π⁺, -N = N-); 252 (n → π⁺, -NO₂).

¹H NMR (DMSO-d₆): 8.77 [1H (s), phenyl, e]; 8.3 [1H (s), phenyl, h]; 8.2 [2H (d), phenyl, g]; 8.0 [2H (d), phenyl, f]; 8.27 [2H (s), phenyl, d]; 7.67 [2H (d), phenyl, b]; 7.57 [2H (d), phenyl, c]; 9.12 [2H (s), OH, a]; 4.1- 4.1 [1H (d), -CH-, i]; 3.1- 3.2 [1H (d), OH, j]; 7.32-7.97 [3H (m), phenyl of TDI, o, m, n]; 8.4 [1H (s), -CONH-, ortho to the CH₃ of TDI, k]; 9.5[1H (s), -CONH-, para to the CH₃ of TDI, l]; [2.4 [3H (s), CH₃ of TDI, p].

¹³C NMR (DMSO-d₆, δ): 60 [-CHOH-, (19)]; 122 (3, 4), 124 (8, 10), 125 (2, 5), 128 (11), 130 (7, 13-18), 132 (12), 140 (6), 149 (1, 9) [aromatic]; 18 [CH₃ of TDI, (28)]; 114,117, 126, 129, 130, 137 [C₁-C₆ of TDI, (22-27)]; 162 [imide carbonyl carbon, ortho to the CH₃ of TDI, (20)]; 160 [imide carbonyl carbon, para to the CH₃ of TDI, (21)].

Fig. 5.6. ¹H NMR assignments of photoproduct of PU5a [PU6a].
5.2.4.3 Photoproduct of PU5b: Poly [1-imido-4-isocyanato-2-methylbenzene -co- cis-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2-nitro-2'-nitrosodiphenyl-carbinol]: PU6b

IR (KBr, cm⁻¹): 3418 [-OH / N-H]; 2924 [-CH-]; 1680 [imide carbonyl]; 1590 [-N = N-]; 1530, 1348 [-NO₂]; 1503 [nitroso].

UV (dioxane, λmax, nm): 372 [π → π⁺, -N = N-]; 254 [n → π⁺, -NO₂].

¹H NMR (DMSO-d₆, δ): 8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.0 [2H (d), phenyl]; 8.27 [1H (s), phenyl]; 7.67 [1H (d), phenyl]; 7.58 [1H (d), phenyl]; 8.17 [1H (s), phenyl]; 7.43 [1H (s), phenyl]; 9.12 [1H (s), OH]; 9.2 [1H (s), OH]; 4 - 4.1 [1H (d), -CH-]; 3.1 - 3.2 [1H (d), OH]; 2.29 [3H (s), CH₃]; 7.32-7.97 [3H (m), phenyl of TDI]; 8.4 [1H (s), -CONH-, ortho to the CH₃ of TDI]; 9.5 [1H (s), -CONH-, para to the CH₃ of TDI]; 2.4 [3H (s), CH₃ of TDI].

¹³C NMR (DMSO-d₆, δ): 20 [methyl]; 60 [-CHOH-]; 116, 120, 122, 124, 125, 128, 130, 133, 149 [aromatic]; 18 [CH₃ of TDI]; 114, 117, 126, 129, 130, 137 [C₁-C₆ of TDI];
5.2.4.4 Photoproduct of PU5c: Poly [1-imido-4-isocyanato-2-methylbenzene -co-cis -
bis (4-hydroxy-3-methylphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU6c

IR (KBr, cm\(^{-1}\)): 3400 [-OH / N-H]; 2924 [-CH-]; 1680 [imide carbonyl]; 1598 [-N = N-];
1530, 1351 [-NO\(_2\)]; 1503 [nitroso].

UV (dioxane, \(\lambda_{\text{max}}, \text{nm}\)): 374 \([\pi \rightarrow \pi^* , -N = N-]\); 252 \([n \rightarrow \pi^* , -NO_2]\).

\(^1\)H NMR (DMSO-d\(_6\), \(\delta\)): 8.77 [1H (s), phenyl]; 8.3 [1H (s), phenyl];
8.2 [2H (d), phenyl]; 8 [2H (d), phenyl]; 8.17 [2H (s), phenyl]; 7.43 [2H (s), phenyl];
9.2 [2H (s), OH]; 4- 4.1 [1H (d), -CH-]; 3.1- 3.2 [1H (d), OH]; 2.29 [6H (s), two CH\(_3\)];
7.32-7.97 [3H (m), phenyl of TDI]; 8.4 [1H (s), -CONH-, ortho to the CH\(_3\) of TDI];
9.5 [1H (s), -CONH-, para to the CH\(_3\) of TDI]; 2.4 [3H (s), CH\(_3\) of TDI].

\(^1\)C NMR (DMSO-d\(_6\), \(\delta\)): 20 [methyl]; 60 [-CHOH-]; 120, 122, 124, 125, 128, 130, 133,
149 [aromatic]; 18 [CH\(_3\) of TDI]; 114,117, 126, 129, 130, 137 [C\(_1\)- C\(_6\) of TDI];
162 [imide carbonyl carbon ortho to the CH\(_3\) of TDI]; 160 [imide carbonyl carbon, para
to the CH\(_3\) of TDI].

5.2.4.5 Results and discussion

The IR, UV-Vis and NMR (\(^1\)H and \(^1\)C) spectra of the photoproducts of PU5a / PU5b /
PU5c revealed that, the photoproducts were characterized by nitro, nitroso, cis-azo,
phenolic and aliphatic alcoholic functional groups. However, the photoreaction was
found to be faster than that for polyurethanes based on IPDI and HDI. The photoproducts
of PU5a / PU5b / PU5c were identified as PU6a / PU6b / PU6c respectively (scheme 5.3).
The \(< M >_n\) and \(< M >_w\) of the photoproducts PU6a / PU6b / PU6c were \(\sim 10952\) and \(\sim\)
21574 respectively. Thus the PDI of the photoproduct is almost the same as that of the starting material. This confirms the absence of photodegradation during photolysis. The results indicate that the photoproducts obtained from PU5a, PU5b and PU5c are of similar type.

**Mechanism**

The spectral data of the photoproducts of PU5a / PU5b / PU5c suggest that the azo group undergoes trans-cis isomerisation and one of the nitro groups is reduced to nitroso and the methylene group is oxidized to carbinol group, as discussed earlier. The molecule then undergoes 0-Fries rearrangement at the urethane bond (scheme 5.3). The sequence of the reaction follows the order: azo < nitro < carbonyl from a consideration of the bond energy of the groups. The Fries rearrangement involves a homolytic cleavage of one of
Scheme 5.3 Mechanism of Phototransformation of PU5a / PU5b / PU5c
the C-O bonds of the urethane part of the molecule. This is followed by the migration of the imide radical formed to the adjacent carbon of the diol component by the homolytic cleavage of a C-H bond. The proton thus formed then migrates to the newly formed carbonyl oxygen.

5.2.4.6 Photolysis of Polyurethanes (PU5a / PU5b / PU5c) of 2, 4-Toluene diisocyanate and 2c / 2d / 2e in acidified 2-propanol

The polyurethane (PU5a / PU5b / PU5c, 500 mg) was dissolved in 1000 mL of pure dry 2-propanol containing 1 mL of conc. H₂SO₄. The solution was irradiated for 14 h and was worked up as before. The residue photoproduct was identified as PU6a / PU6b / PU6c corresponding to PU5a / PU5b / PU5c respectively on the basis of spectral data:

5.2.4.7 Photoproduct of PU5a: Poly [1-imido-4-isocyanato-2-methylbenzene -co-cis-bis (4-hydroxyphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU6a

IR (KBr, cm⁻¹): 3400 [-OH / N-H]; 2924 [-CH-]; 1680 [imide carbonyl]; 1598 [-N = N-]; 1530, 1346 [-NO₂]; 1504 [nitroso].

UV (dioxane, λmax, nm): 369 [π → π⁺, -N = N-]; 252 [n → π⁺, -NO₂].

¹H NMR (DMSO-d₆, δ): 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.3 [1H (s), phenyl]; 8 [2H (d), phenyl]; 8.27 [2H (s), phenyl]; 7.67 [2H (d), phenyl]; 7.58 [2H (d), phenyl]; 9.12 [2H (s), OH]; 4- 4.1 [1H (d), -CH-]; 3.1- 3.2 [1H (d), OH]; 7.32-7.97 [3H (m), phenyl of TDI]; 8.4 [1H (s), -CONH-, ortho to the CH₃ of TDI]; 9.5 [1H (s), -CONH-, para to the CH₃ of TDI]; 2.4 [3H(s), CH₃ of TDI].

¹³C NMR (DMSO-d₆, δ): 60 [-CHOH-]; 122, 124, 125, 128, 130, 132, 140, 149 [aromatic]; 18 [CH₃ of TDI]; 114,117, 126, 129, 130, 137 [C₁-C₆ of TDI];
5.2.4.8 Photoproduct of PU5b: Poly [1-imido-4-isocyanato-2-methylbenzene -<i>co</i>- cis-
-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2-nitro-2'-nitrosodiphenyl
carbinol]: PU6b

IR (KBr, cm⁻¹): 3418 [-OH / N-H]; 2924 [-CH-]; 1680 [imide carbonyl]; 1590 [-N = N-];
1530, 1349 [-NO₂]; 1503 [nitroso].

UV (dioxane, λₘₐₓ, nm): 374 [π → π⁺, -N = N-]; 253 [n → π⁺, -NO₂].

¹H NMR (DMSO-d₆, δ): 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl];
8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl]; 8.27 [1H (s), phenyl]; 7.67 [1H (d), phenyl];
7.58 [1H (d), phenyl]; 8.17 [1H (s), phenyl]; 7.43 [1H (s), phenyl]; 9.12 [1H (s), OH];
9.2 [1H (s), OH]; 4- 4.1 [1H (d), -CH-]; 3.1- 3.2 [1H (d), OH]; 2.29 [3H (s), CH₃];
7.32-7.97 [3H (m), phenyl of TDI]; 8.4 [1H (s), -CONH- , ortho to the CH₃ of TDI];
9.5 [1H (s), -CONH- , para to the CH₃ of TDI]; 2.4 [3H (s), CH₃ of TDI].

¹³C NMR (DMSO-d₆, δ): 20 [methyl]; 60 [-CHOH-]; 116, 120, 122, 124, 125, 128, 130,
133, 149 [aromatic]; 18 [CH₃ of TDI]; 114,117, 126, 129, 130,137 [C₁- C₆ of TDI];
162 [imide carbonyl carbon, ortho to the CH₃ of TDI]; 160 [imide carbonyl carbon, para
to the CH₃ of TDI].

5.2.4.9 Photoproduct of PU5c: Poly [1-imido-4-isocyanato-2-methylbenzene -<i>co</i>-cis-
bis (4-hydroxy-3-methylphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU6c

IR (KBr, cm⁻¹): 3380 [-OH / N-H]; 2924 [-CH-]; 1680 [imide carbonyl]; 1595 [-N = N-];
1531, 1352 [-NO₂]; 1504 [nitroso].

UV (dioxane, λₘₐₓ, nm): 374 [π → π⁺, -N = N-]; 253 [n → π⁺, -NO₂]
$^1$H NMR (DMSO-$d_6$, $\delta$): 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl];
8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl]; 8.17 [2H (s), phenyl]; 7.43 [2H (s), phenyl];
9.2 [2H (s), OH]; 4- 4.1 [1H (d), -CH-]; 3.1- 3.2 [1H (d), OH]; 2.29 [6H (s), two CH$_3$];
7.32-7.97 [3H (m), phenyl of TDI]; 8.4 [1H (s), -CONH-, ortho to the CH$_3$ of TDI];
9.5 [1H (s), -CONH-, para to the CH$_3$ of TDI]; 2.4 [3H (s), CH$_3$ of TDI].

$^{13}$C NMR (DMSO-$d_6$, $\delta$): 20 [methyl]; 60 [-CHOH-]; 120, 122, 124, 125, 128, 130, 133,
149 [aromatic]; 18 [CH$_3$ of TDI]; 114, 117, 126, 129, 130, 137 [C$_1$- C$_6$ of TDI];
162 [imide carbonyl carbon, ortho to the CH$_3$ of TDI]; 160 [imide carbonyl carbon, para
to the CH$_3$ of TDI].

5.2.4.10 Results and discussion

The IR, UV-Vis and NMR ($^1$H and $^{13}$C) spectra of the photoproducts of PU5a / PU5b /
PU5c revealed that the photoreactions were similar to that as before. However, in
acidified 2-propanol the reaction took place at a faster rate than that in neutral 2-
propanol. The photoproducts of PU5a / PU5b /PU5c were identified as PU6a / PU6b /
PU6c respectively.

5.2.4.11 Photolysis of Polyurethanes (PU5a / PU5b / PU5c) of 2, 4-Toluene
diisocyanate and 2c / 2d / 2e in neutral Ethyl acetate

The polyurethane (PU5a / PU5b / PU5c, 500 mg) was dissolved in 1000 mL of pure
dry ethyl acetate. The solution was irradiated for 16 h and was worked up as before. The
residue photoproducts were identified as PU6a / PU6b / PU6c corresponding to PU5a /
PU5b / PU5c respectively, on the basis of spectral data:
5.2.4.12 Photoproduct of PU6a: Poly [1-imido-4-isocyanato-2-methylbenzene -co-cis
bis (4-hydroxyphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU6a
IR (KBr, cm⁻¹): 3381 [-OH / N-H]; 2923 [-CH-]; 1680 [imide carbonyl]; 1598 [-N = N-];
1530, 1347 [-NO₂]; 1504 [nitroso].
UV (dioxane, λmax, nm): 370 [π → π⁺, -N = N-]; 252 [n → π⁺, -NO₂];
¹H NMR (DMSO-d₆, δ): 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl];
8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl]; 8.27 [2H (s), phenyl]; 7.67 [2H (d), phenyl];
7.58 [2H (d), phenyl]; 9.12 [2H (s), OH]; 4.4 [1H (d), -CH-]; 3.1-3.2 [1H (d), OH];
7.32-7.97 [3H (m), phenyl of TDI]; 8.4 [1H (s), -CONH-, ortho to the CH₃ of TDI];
9.5 [1H (s), -CONH-, para to the CH₃ of TDI]; 2.4 [3H (s), CH₃ of TDI].
¹³C NMR (DMSO-d₆, δ): 60 [-CHOH-]; 122, 124, 125, 128, 130, 132, 140,
149 [aromatic]; 18 [CH₃ of TDI]; 114, 117, 126, 129, 130, 137 [C₁-C₆ of TDI];
162 [imide carbonyl carbon, ortho to the CH₃ of TDI]; 160 [imide carbonyl carbon, para
to the CH₃ of TDI].

5.2.4.13 Photoproduct of PU6b: Poly [1-imido-4-isocyanato-2-methylbenzene -co-cis-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2-nitro-2'-nitrosodiphenyl
carbinol]: PU6b
IR (KBr, cm⁻¹): 3418 [-OH / N-H]; 2924 [-CH-]; 1680 [imide carbonyl]; 1590 [-N = N-];
1530, 1349 [-NO₂]; 1504 [nitroso].
UV (dioxane, λmax, nm): 372 [π → π⁺, -N = N-]; 253 [n → π⁺, -NO₂];
¹H NMR (DMSO-d₆, δ): 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl];
8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl]; 8.27 [1H (s), phenyl]; 7.67 [1H (d), phenyl];
7.58 [1H (d), phenyl]; 8.17 [1H (s), phenyl]; 7.43 [1H (s), phenyl]; 9.12 [1H (s), OH];
9.2 [1H (s), OH]; 4- 4.1 [1H (d), -CH-]; 3.1- 3.2 [1H (d), OH]; 2.29 [3H (s), CH3]; 7.32-7.97 [3H (m), phenyl of TDI]; 8.4 [1H (s), -CONH- , ortho to the CH3 of TDI];

9.5 [1H (s), -CONH- , para to the CH3 of TDI]; 2.4 [3H (s), CH3 of TDI].

$^1$C NMR (DMSO-d$_6$, δ): 20 [methyl]; 60 [-CHOH-]; 116, 120, 122, 124, 125, 128, 130, 133, 149 [aromatic]; 18 [CH$_3$ of TDI]; 114, 117, 126, 129, 130, 137 [C$_1$- C$_6$ of TDI];

162 [imide carbonyl carbon, ortho to the CH$_3$ of TDI]. 160 [imide carbonyl carbon, para to the CH$_3$ of TDI].

5.2.4.14 Photoprod uct of PU5c: Poly [1-imido-4-isocyanato-2-methylbenzene -co-
cis-bis (4-hydroxy- 3-methylphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU6c

IR (KBr, cm$^{-1}$): 3380 [-OH / N-H]; 2924 [-CH-]; 2924 [imide carbonyl]; 1590 [-N = N-];

1532, 1352 [-NO$_2$]; 1503 [nitroso].

UV (dioxane, $\lambda$max, nm): 375 [$\pi \rightarrow \pi^*$, -N = N-]; 252 [$n \rightarrow \pi^*$, -NO$_2$].

$^1$H NMR (DMSO-d$_6$, δ): 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl];

8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl]; 8.17 [2H (s), phenyl]; 7.43 [2H (s), phenyl];

9.2 [2H (s), OH]; 4- 4.1 [1H (d), -CH-]; 3.1- 3.2 [1H (d), OH]; 2.29 [6H (s), two CH$_3$];

7.32-7.97 [3H (m), phenyl of TDI]; 8.4 [1H (s), -CONH- , ortho to the CH$_3$ of TDI];

9.5 [1H (s), -CONH- , para to the CH$_3$ of TDI]; 2.4 [3H (s), CH$_3$ of TDI].

$^1$C NMR (DMSO-d$_6$, δ): 20 [methyl]; 60 [-CHOH-]; 120, 122, 124, 125, 128, 130, 133, 149 [aromatic]; 18 [CH$_3$ of TDI]; 114, 117, 126, 129, 130, 137 [C$_1$- C$_6$ of TDI];

162 [imide carbonyl carbon, ortho to the CH$_3$ of TDI]. 160 [imide carbonyl carbon, para to the CH$_3$ of TDI].
5.2.4.15 Results and discussion

The IR, UV-Vis and NMR (\(^1\)H and \(^13\)C) spectra of the photoproduct of PU5a / PU5b / PU5c revealed that the photoproducts were similar to that as before. However, the photoreaction took place at a faster rate than that in 2-propanol. The photoproducts of PU5a / PU5b / PU5c were identified as PU6a / PU6b / PU6c respectively.

5.2.4.16 Photolysis of Polyurethanes (PU5a / PU5b / PU5c) of 2, 4-Toluene diisocyanate and 2c / 2d / 2e in acidified Ethyl acetate

The polyurethane (PU5a / PU5b / PU5c, 500 mg) was dissolved in pure dry ethyl acetate (1000 mL), containing 1mL of conc.H2SO4. The solution was irradiated for 12 h and was worked up as before. The residue photoproduct was identified as PU6a / PU6b / PU6c corresponding to PU5a / PU5b / PU5c respectively on the basis of spectral data:

5.2.4.17 Photoproduct of PU5a: Poly [1-imido-4-isocyanato-2-methylbenzene -co-cis bis (4-hydroxyphenylazo)-2-nitro-2'-nitrosodiphenylcarbinol]: PU6a

IR (KBr, cm\(^{-1}\)): 3348 [-OH / N-H]; 2924 [-CH-]; 1680 [imide carbonyl]; 1595 [-N = N-]; 1530, 1346 [-N02]; 1503 [nitroso].

UV (dioxane, \(\lambda_{max}\), nm): 369 [\(\pi \rightarrow \pi^*\), -N = N-]; 252 [n \(\rightarrow \pi^*\), -NO2];

\(^1\)H NMR (DMSO-d\(_6\), \(\delta\)): 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl]; 8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl]; 8.27 [2H (s), phenyl]; 7.67[2H (d), phenyl]; 7.58 [2H (d), phenyl]; 9.12 [2H (s), OH]; 4- 4.1 [1H (d), -CH-]; 3.1- 3.2 [1H (d), OH];

7.32-7.97 [3H (m), phenyl of TDI]; 8.4 [1H (s), -CONH-, ortho to the CH3 of TDI];

9.5 [1H (s), -CONH-, para to the CH3 of TDI]; 2.4 [3H (s), CH3 of TDI].

\(^13\)C NMR (DMSO-d\(_6\), \(\delta\)): 60 [-CHOH-]; 122, 124, 125, 128, 130, 132, 140, 149 [aromatic]; 18 [CH3 of TDI]; 114,117, 126, 129, 130, 137 [C1- C6 of TDI];
162 [imide carbonyl carbon, ortho to the CH$_3$ of TDI]; 160 [imide carbonyl carbon, para to the CH$_3$ of TDI].

5.2.4.18 Photoproduct of PU5b: Poly [1-imido-4-isocyanato-2-methylbenzene -co-cis-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2-nitro-2'-nitrosodiphenyl carbinol]: PU6b

IR (KBr, cm$^{-1}$): 3417 [-OH / N-H]; 2924 [-CH-]; 1680 [imide carbonyl]; 1590 [-N = N-]; 1530, 1349 [-N$_2$O$_2$]; 1503 [nitroso].

UV (dioxane, $\lambda_{max}$, nm): 372 [$\pi \rightarrow \pi^*$, -N = N-]; 252 [$n \rightarrow \pi^*$, -NO$_2$].

$^1$H NMR (DMSO-d$_6$, $\delta$): 8.77 [1 H (s), phenyl]; 8.2 [2 H (d), phenyl]; 8.3 [1 H, (s), phenyl]; 8.0 [2 H (d), phenyl]; 8.27 [1 H (s), phenyl]; 7.67[1 H (d), phenyl]; 7.58 [1 H (d), phenyl]; 8.17 [1 H (s), phenyl]; 7.43 [1 H (s), phenyl]; 9.12 [1 H (s), OH]; 9.2 [1 H (s), OH]; 4- 4.1 [1 H (d), -CH-]; 3.1- 3.2 [1 H (d), OH]; 2.29 [3 H (s), CH$_3$]; 7.32-7.97 [3 H (m), phenyl of TDI]; 8.4 [1 H (s), -CONH-, ortho to the CH$_3$ of TDI]; 9.5 [1 H (s), -CONH-, para to the CH$_3$ of TDI]; 2.4 [3 H (s), CH$_3$ of TDI].

$^{13}$C NMR (DMSO-d$_6$, $\delta$): 20 [methyl]; 60 [-CHOH-]; 116, 120, 122, 124, 125, 128, 130, 133, 149 [aromatic]; 18 [CH$_3$ of TDI]; 114,117, 126, 129, 130,137 [C$_1$- C$_6$ of TDI]; 162 [imide carbonyl carbon, ortho to the CH$_3$ of TDI]; 160 [imide carbonyl carbon, para to the CH$_3$ of TDI].

5.2.4.19 Photoproduct of PU5c: Poly [1-imido-4-isocyanato-2-methylbenzene -co-cis-bis (4-hydroxy-3-methylphenylazo)-2-nitro-2'-nitrosodiphenyl carbinol]: PU6c

IR (KBr, cm$^{-1}$): 3380 [-OH / N-H]; 2924 [-CH-]; 1680 [imide carbonyl]; 1590 [-N = N-]; 1532, 1352 [-NO$_2$]; 1503 [nitroso].

UV (dioxane, $\lambda_{max}$, nm): 375 [$\pi \rightarrow \pi^*$, -N = N-]; 252 [$n \rightarrow \pi^*$, -NO$_2$].
1H NMR (DMSO-d$_6$, $\delta$): 8.77 [1H (s), phenyl]; 8.2 [2H (d), phenyl];
8.3 [1H (s), phenyl]; 8.0 [2H (d), phenyl]; 8.17 [2H (s), phenyl]; 7.43 [2H (s), phenyl];
9.2 [2H (s), OH]; 4- 4.1 [1H (d), -CH-]; 3.1- 3.2 [1H (d), OH]; 2.29 [6H (s), two CH$_3$];
7.32-7.97 [3H (m), phenyl of TDI]; 8.4 [1H (s), -CONH-, ortho to the CH$_3$ of TDI];
9.5 [1H (s), -CONH-, para to the CH$_3$ of TDI]; 2.4 [3H (s), CH$_3$ of TDI].

$^{13}$C NMR (DMSO-d$_6$, $\delta$): 20 [methyl]; 60 [-CHOH-]; 120, 122, 124, 125, 128, 130, 133,
149 [aromatic]; 18 [CH$_3$ of TDI]; 114, 117, 126, 129, 130, 137 [C$_1$- C$_5$ of TDI];
162 [imide carbonyl carbon, ortho to the CH$_3$ of TDI]; 160 [imide carbonyl carbon, para
to the CH$_3$ of TDI].

5.2.4.20 Results and discussion
The IR, UV-Vis and NMR (1H and $^{13}$C) spectra of the photoproducts of PU5a / PU5b /
PU5c revealed that the photoproducts were similar to that as before. However, in
acidified ethyl acetate, the reaction was a little faster than that in neutral ethyl acetate.
The photoproducts of PU5a / PU5b / PU5c were identified as PU6a / PU6b / PU6c
respectively.

5.3 CONCLUSIONS
Polyurethanes containing 2-nitrobenzyl and azo chromophores in the main chain have
been synthesized and characterized. The diisocyanate components of the polymer are
IPDI, HMDI and 2, 4-TDI. The photoreaction of the monomers for these polymers such
as bis (4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane, 4-hydroxy-3-methyl
phenylazo-4'-hydroxyphenylazo-2,2'-dinitrodiphenylmethane and bis(4-hydroxy-3-
methylphenylazo)-2,2'-dinitrodiphenylmethane have been carried out in neutral and
acidified protic and aprotic solvents. In these monomers, one of the nitro groups
undergoes reduction to nitroso group and the –CH₂ group is partially oxidised to –CHOH group, whereas the azo group undergoes trans to cis isomerisation. In the polyurethanes of these monomers, there occurs photo-Fries rearrangement at the urethane carbonyl group without degradation in the case of TDI based polyurethanes, and no change at the urethane group in IPDI and HMDI based polyurethanes, in addition to the above changes in the monomers, when the reaction has been carried out in neutral and acidic protic and aprotic solvents. The absence of photodegradation of the polyurethanes is further confirmed by almost the same value of the polydispersity index of the photoproducts with that of the starting compounds, determined through GPC. The results of this study reveal that the photochemistry of the polyurethanes is similar to that reported in this thesis for the low molecular weight bis (4-hydroxyphenylazo)-2, 2′-dinitrodiphenylmethane derivatives.

The future chemical containers for the storage of light energy and the mediums of light energy for chemical functions are chemical substances that exhibit photo-induced structural changes. Since the conformation of azobenzene containing polymers can be controlled by using photoinduced changes of the azo benzene moiety, the azo polymers may lead to the possibility of light-controlled chemical functions, viz., “on-off light switch”. Such photoresponsive synthetic polymers can transfer light energy into a change in the conformation of the polymer. By a structural change of the chromophore, the light is stored at once and then transferred into the polymer chain. This causes a reversible conformational change and can produce a concomitant change in properties of the polymer solutions and solids. Thus by using photoresponsive trigger chromophores, the properties of polymers may be controlled by photo-irradiation.
The photoresponsive polyurethanes reported in this thesis represent a new field of speciality polymers. The photo-isomerisation of the azo-benzene chromophores in the repeating unit, using high intensity light can result in a permanent storage of information, since photo-isomerisation of both chromophores in the molecule brings about a conformational restriction which hinders the cis-trans isomerisation in both chromophores. Moreover, the phototransformations of the polyurethanes can create a large polarity difference between the unirradiated and irradiated polymer. Using this system, it will be possible to record images by UV-light. Therefore, the polyurethanes can find application in constructing photoactive devices in several fields, such as printing, photocopying and in micro-structuring technologies such as micro-electronics and micro-optics.

5.4 References


