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Synthesis and Properties of Polyurethanes of Hexamethylene Di-Isocyanate with Multifunctional Chromophores in the Main Chain

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Various polyurethanes containing photoactive bis(azo) and bis(o-nitrobenzyl) groups in the main chain were synthesized by polyaddition reactions of diols such as bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane, 4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2,2'-dinitrodiphenylmethane and bis(4-hydroxy-3-methylphenylazo)-2,2'-dinitrodiphenylmethane with hexamethylene di-isocyanate (HMDI), in dimethyl acetamide (DMAc) in the presence of di-n-butyltin dilaurate (DBTDL) as catalyst. All of them were characterized by IR, UV-vis, ¹H NMR and ¹³C NMR spectra and also by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC).

Keywords: bis(azo), bis(o-nitrobenzyl), hexamethylene di-isocyanate, polyaddition, polyurethanes

INTRODUCTION

Polyurethanes have attracted great interest in recent years because of their wide range of properties [1–3] and applications. The azobenzene-bearing polyurethanes, in particular, are predicted to be of use in the field of nonlinear optics, optical data storage or processing and biomedical goods [4–7]. 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 [8,9].

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The commercial applications and forecasts for the use of polyurethanes have been reviewed [10].

This paper is a continuation of our earlier work [11] and was undertaken with a view to study the effect of azo chromophore on *o*-nitrobenzyl group in the polyurethane backbone. In this article, we present the synthesis and characterization of polyurethanes of HMDI with diols such as bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane, 4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2,2'-dinitrodiphenylmethane and bis(4-hydroxy-3-methylphenylazo)-2,2'-dinitrodiphenylmethane.

MATERIALS

Hexamethylene di-isocyanate (Fluka) and the catalyst, di-*n*-butyltin dilaurate (Fluka) were used as received without purification. Solvents such as dimethyl acetamide (Merck), dioxane (Merck) and methanol (Merck) were purified by standard procedures. The diols were purified by column chromatography using 100–200 mesh silica gel and an appropriate mixture of benzene and ethylacetate-benzene mixture for elution. The solvents were distilled before use for column chromatography.

EXPERIMENTAL

Synthesis of Monomers

The aromatic diols for polyurethane synthesis were prepared as per the scheme in Figure 1 by adopting a reported procedure [11]. The monomers used are bis(4-hydroxyphenylazo)-2, 2'-dinitrodiphenylmethane [1c], 4-hydroxy-3-methylphenyl-azo-4'-hydroxyphenylazo-2, 2'-dinitrodiphenylmethane [1d], bis(4-hydroxy-3-methylphenylazo)-2, 2'-dinitrodiphenyl-methane [1e], and HMDI.

Synthesis of Polyurethanes based on HMDI

Polyurethane of Hexamethylene Di-Isocyanate and bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane (PU 1c): Poly[1,6-diisocyanatohexane-co-bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane]

A solution of bis(4-hydroxyphenylazo)-2, 2'-dinitrodiphenylmethane (6 mmol, 2.988 g) in HPLC grade DMAc (50 mL) was taken in a 500 mL RB flask. To this solution, hexamethylene di-isocyanate (6.06 mmol,

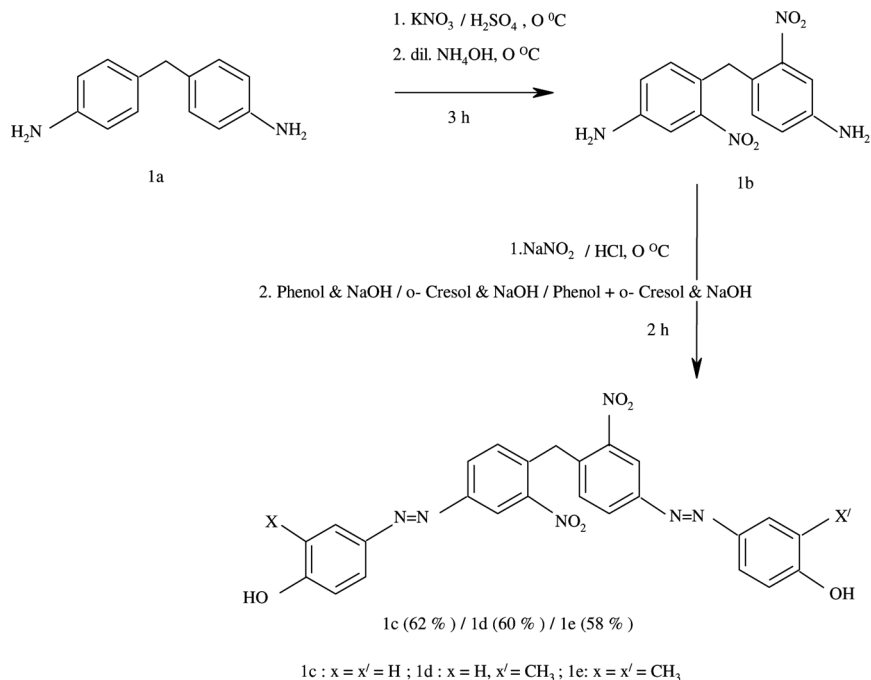


FIGURE 1 Scheme for the synthesis of aromatic diols.

1.1 mL) in DMAc (10 mL) and DBTDL (4 drops) were added with stirring. The reaction mixture was heated at 70°C for 20 h. The polymer was precipitated by pouring the reaction mixture to a large excess of water. The polyurethane thus obtained was washed with methanol and dried under vacuum.

Polyurethane of Hexamethylene Di-Isocyanate and 4-Hydroxy-3-methyl-phenylazo-4'-hydroxyphenylazo-2,2'-dinitrodiphenyl methane (PU 1d): Poly [1,6-diisocyanatohexane-co-4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2, 2'-dinitrodiphenylmethane]

To a solution of 4-hydroxy-3-methylphenylazo-4'-hydroxyphenylazo-2,2'-dinitrodiphenylmethane (6 mmol, 3.072 g) in HPLC grade DMAc (40 mL), HMDI (1.1 mL, 6.6 mmol) in DMAc (5 mL) and DBTDL (4 drops) were added with stirring. The mixture was heated at 70°C for 20 h. The reaction mixture was poured into excess of water and the precipitated polyurethane was separated, washed with methanol and vacuum-dried.

Polyurethane of Hexamethylene Di-Isocyanate and bis(4-hydroxy-3-methyl-phenylazo)-2,2'-dinitrodiphenylmethane (PU 1e): Poly [1, 6-di-isocyanatohexane-co-bis(4-hydroxy-3-methylphenylazo)-2,2'-dinitrodiphenylmethane]

A solution of bis(4-hydroxy-3-methylphenylazo)-2, 2'-dinitrodiphenylmethane (4.5 mmol, 2.37 g) in HPLC grade DMAc (40 mL) upon reaction with HMDI (0.825 mL, 4.95 mmol) in DMAc (10 mL) in the presence of DBTDL (3 drops) at 70°C for 20 h yielded PU1e.

MEASUREMENTS

IR spectra were recorded on IFS 66U FTIR spectrometer. ^1H NMR spectra were recorded on JEOL model GSX 400 MHz spectrometer and ^{13}C NMR spectra were obtained using Bruker 300 MHz spectrometer with TMS as internal standard. UV-vis spectra were obtained using Shimadzu UV-2100 spectrophotometer. The purity of the crude and recrystallized products was monitored both by UV and TLC measurements. TLC was performed on a 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.

Thermogravimetric analysis (TGA) of all the polyurethanes was conducted using the Mettler Toledo Star system in an atmosphere of nitrogen. The sample weight was 3.5–4 mg. The heating rate was 20°C/min and the temperature range was 50–600°C. 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 ($\langle M \rangle_w$ and $\langle M \rangle_n$) of the polyurethanes were determined by GPC with a Waters liquid chromatograph equipped with a series of μ -Styragel columns (HR1, HR4, HR5 and HR5E), an isocratic high-performance liquid chromatography pump (Waters 1515), an autosampler (Waters 717), and a 2410 differential refractometer. DMAc was used as the eluent and a flow rate of 1 mL/min was maintained in all runs. Molecular weight calibration was performed with polystyrene standards with molecular weights of 1.024×10^3 to $3.9 \times 10^6 \text{ g mol}^{-1}$. Universal calibration was performed with Mark-Houwink-Sakurada polyurethane constants: $K = 2.9 \times 10^{-4} \text{ dL g}^{-1}$ and $a = 0.70$ [12,13].

RESULTS AND DISCUSSION

The scheme for the synthesis of polyurethanes from HMDI and the diols is shown in Figure 2. The properties of the polyurethanes are given in Table 1.

The IR spectra of the polyurethanes PU1c, PU1d and PU1e showed characteristic strong absorption bands at 3296, 3321 and 3325 cm^{-1} , respectively, due to hydrogen-bonded N-H stretching vibration and at 1689, 1720 and 1723 cm^{-1} , respectively, due to C=O stretching vibration of the urethane bond. An absorption band at $\sim 1530 \text{ cm}^{-1}$ was due to the C-N-H bending of the urethane group and the asymmetric stretching of the $-\text{NO}_2$ group. Absorption bands due to CH_2 stretching at 2927, 2932 cm^{-1} and 2854, 2856 cm^{-1} , $-\text{NO}_2$ group at $\sim 1530 \text{ cm}^{-1}$, $\sim 1350 \text{ cm}^{-1}$, azo group at 1604, 1616 and 1618 cm^{-1} , and the C-O-C stretching of the urethane at 1234, 1236 and 1238 cm^{-1} , respectively, were observed.

In the UV spectra of the above polyurethanes, absorption due to $n \rightarrow \pi^*$ of $-\text{NO}_2$ group occurred at 250, 251 and 253 nm, and the absorption due to $\pi \rightarrow \pi^*$ of azo group occurred at 371, 375 and 377 nm, respectively. However, the absorption band due to the urethane carbonyl could not be observed. This might be due either to overlapping between the carbonyl and the nitro absorption or shortening of the absorption wavelength.

The ^1H NMR spectra of the polymers based on HMDI showed peak at δ 6.9 due to NH proton of the urethane group. The aromatic protons showed peaks between 8.77 and 8. The peak at δ 2.9 was due to

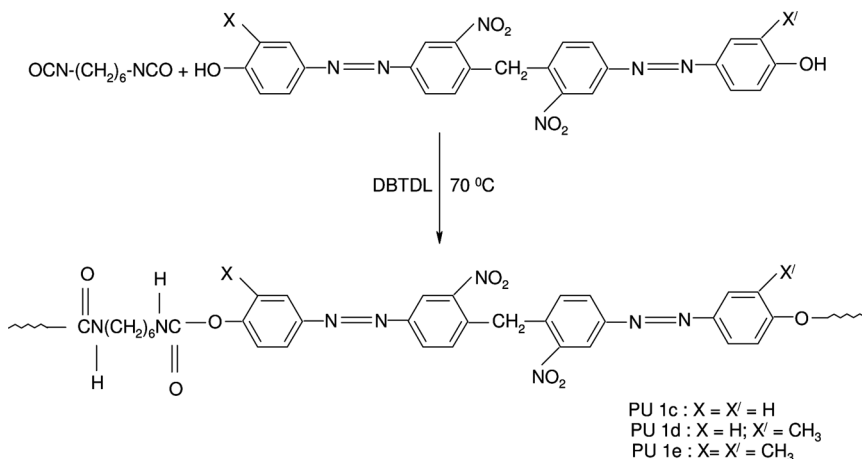


FIGURE 2 Scheme for the synthesis of polyurethanes.

TABLE 1 Properties of Polyurethanes

Polymer code no.	PU1c	PU1d	PU1e
Yield (%)	82	80	85
Color	Reddish-brown	Yellowish-brown	Yellowish-brown
Molec.wt. (M_n / M_w)	12512/24404	12526/24418	12540/24432
Spectral data			
IR (KBr, cm^{-1})	3296 [N-H]; 2927, 2854 [-CH ₂ -]; 1689 [urethane carbonyl]; 1604 [-N=N-]; 1531, 1346 [-NO ₂]; 1234 [c-o-c in -cooc- of PU]	3321 [N-H]; 2932, 2856 [-CH ₂]; 1720 [urethane carbonyl]; 1616 [-N=N-]; 1531, 1349 [-NO ₂]; 1236 [c-o-c in -cooc- of PU]	3325 [N-H]; 2932, 2854 [CH ₂]; 1723 [urethane carbonyl]; 1618 [-N=N-]; 1531, 1350 [-NO ₂]; 1238 [c-o-c in -cooc- of PU]
UV (dioxane, λ_{max} , nm)	371 [$\pi \rightarrow \pi^*$, -N=N-]; 250 [$n \rightarrow \pi^*$, -NO ₂]	375 ($\pi \rightarrow \pi^*$, -N=N-); 251 ($n \rightarrow \pi^*$, -NO ₂)	377 [$\pi \rightarrow \pi^*$, -N=N-]; 253 [$n \rightarrow \pi^*$, -NO ₂]
¹ H NMR (DMSO-d ₆ , δ)	8.77 [2H (s), ph]; 8.2 [2H (d), ph]; 8 [2H (d), ph]; 8.47 [4H (d), ph]; 8.15 [4H (d), ph]; 6.9 [-OCONH-]; 2.9 [2H(s), Ph-CH ₂ -Ph]; 1.18, 1.9, 2.75 [H of HMDI].	8.77 [2H (s), ph]; 8.2 [2H (d), ph]; 8 [2H (d), ph]; 8.47 [2H (d), ph]; 8.15 [2H (d), ph]; 8.37 [1H (d), ph]; 8.1 [1H (d), ph]; 8.05 [1H (s), ph]; 6.9 [-OCONH-]; 2.9 [2H (s), Ph-CH ₂ -Ph]; 2.29 [3H (s), CH ₃]; 1.18, 1.9, 2.75 [H of HMDI].	8.77 [2H (s), ph]; 8.2 [2H (d), ph]; 8 [2H (d), ph]; 8.37 [2H (d), ph]; 8.1 [2H (d), ph]; 8.05 [2H (s), Ph]; 6.9 [-OCONH-]; 2.9 [2H (s), Ph-CH ₂ -Ph]; 2.29, [6H(s), two CH ₃]; 1.18, 1.9, 2.75 [H of HMDI].
¹³ C NMR (DMSO-d ₆ , δ)	32 [CH ₂], 121, 125, 127, 135, 137, 139, 144, 152, 153, 170 [all aromatic]; 40.12, 30.23, 26.01 [CH ₂ of HMDI]; 157.7 [-OCONH].	20 [CH ₃]; 32 [CH ₂]; 122, 126, 128, 130, 132, 135, 138, 146, 148, 151, 152, 153, 170 [aromatic]; 40.12, 30.23, 26.01 [CH ₂ of HMDI]; 157.7 [-OCONH].	20 [CH ₃]; 32 [CH ₂]; 122, 128, 130, 131, 135, 137, 139, 146, 152, 154, 170 [aromatic]; 40.12, 30.23, 26.01 [CH ₂ of HMDI]; 157.7 [-OCONH].

methylene proton of Ph-CH₂-Ph. The peaks at δ 1.18, 1.9 and 2.75 were due to protons of HMDI.

In the ¹³C NMR spectra of the polymers, the urethane carbonyl carbon gave resonance signal at δ 157.7. The signals between δ 26.01 and 40.12 were due to the carbons of HMDI. The signal at δ 32 was due to the methylene carbon of Ph-CH₂-Ph. The signals due to aromatic carbons were observed between δ 121 and 170.

The polyurethanes PU1c, PU1d and PU1e showed glass transition temperatures at 110 °C, 115°C and 118°C and melting points at 289°C, 294°C and 297°C, respectively. The increase in T_g and T_m values from PU1c, PU1d to PU1e indicates that with an 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. <M>_n and <M>_w of PU1c were 12512 and 24404, that of PU1d were 12526 and 24418 and that of PU1e were 12540 and 24432, respectively, with a polydispersity index of ~1.95.

CONCLUSION

The polyurethanes synthesized from aromatic diols containing bis (azo) and o-nitrobenzyl chromophores with HMDI 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. These polyurethanes can be considered as promising photoactive polymer materials.

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