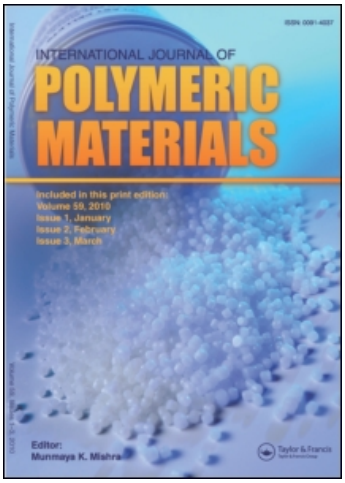


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Synthesis and Characterization of Novel Colored Polyurethanes

M. G. Patel[a]; K. R. Desai[a]; H. S. Patel[b]
[a] Department of Chemistry, South Gujarat University, Surat, Gujarat, India [b] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

To cite this Article Patel, M. G. , Desai, K. R. and Patel, H. S.(2005) 'Synthesis and Characterization of Novel Colored Polyurethanes', International Journal of Polymeric Materials, 54: 6, 519 — 526
To link to this Article: DOI: 10.1080/00914030590913123
URL: http://dx.doi.org/10.1080/00914030590913123

International Journal of Polymeric Materials, 54:519–526, 2005

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030590913123

Taylor & Francis
Taylor & Francis Group

Synthesis and Characterization of Novel Colored Polyurethanes

M. G. Patel
K. R. Desai
Department of Chemistry, South Gujarat University,
Surat, Gujarat, India

H. S. Patel
Department of Chemistry, Sardar Patel University,
Vallabh Vidyanagar, Gujarat, India

Azo disperse dyes containing N, N-diethylol group have been prepared and each dye was polycondensed with 4,4′ -Diphenyl methane diisocyanate. The resultant colored polyurethanes were characterized by nitrogen content, IR spectral studies, number average molecular weight ($\bar{M}n$), estimated by nonaqueous conductometric titration, and thermogravimetry. The electrical conductivity of all the polyurethanes was measured at room temperature.

Keywords: polyurethanes, IR spectral studies, number average molecular weight ($\bar{M}n$), thermogravimetric, electrical conductivity

INTRODUCTION

Polyurethanes are known as commercial polymers. They are produced by the reaction between diols and diisocyanates. In terms of application, they find a number of applications like fibers and film [1], paints lacquers [2], adhesives [3,4], foam [5,6], and elastomer [7,8]. By compounding with additives the polyurethanes are processed into

Received 21 August 2003; in final form 20 October 2003.

The authors are thankful to Atul Products Ltd., Atul for providing chemicals and Garda Chemicals, Panoli Gidc, Ankleswer for providing the thermal studies. The authors are also thankful to South Gujarat University, Surat for providing the research facility.

Address Correspondence to Prof. K. R. Desai, Head of Department of Chemistry, South Gujarat University, Surat, Gujarat 395007, India. E-mail: k_r_desai@rediffmail.com

the referenced articles. One of the additives is the pigment required for decorative appearance of end products. The area in which the polyurethanes are themselves colored has not received any attention academically and technically. Thus, it was thoughtwise to explore the field of colored polyurethane. In the field of dyes, many disperse azo dyes contain diethylol functional groups. If these dyes polymerize through these hydroxy groups with diisocyanate they may afford colored polyurethanes.

Thus, it was thought interesting to study the polyurethanes based on azo dispersed dyes containing diethylol group. The synthetic work is shown in Scheme 1.

EXPERIMENTAL

Materials

All the chemicals used were of analytical grade or laboratory grade.

Synthesis of Azo Disperse Dyes

The azo disperse dyes having structures shown in Scheme 1; they were prepared by the method reported in this literature [9].

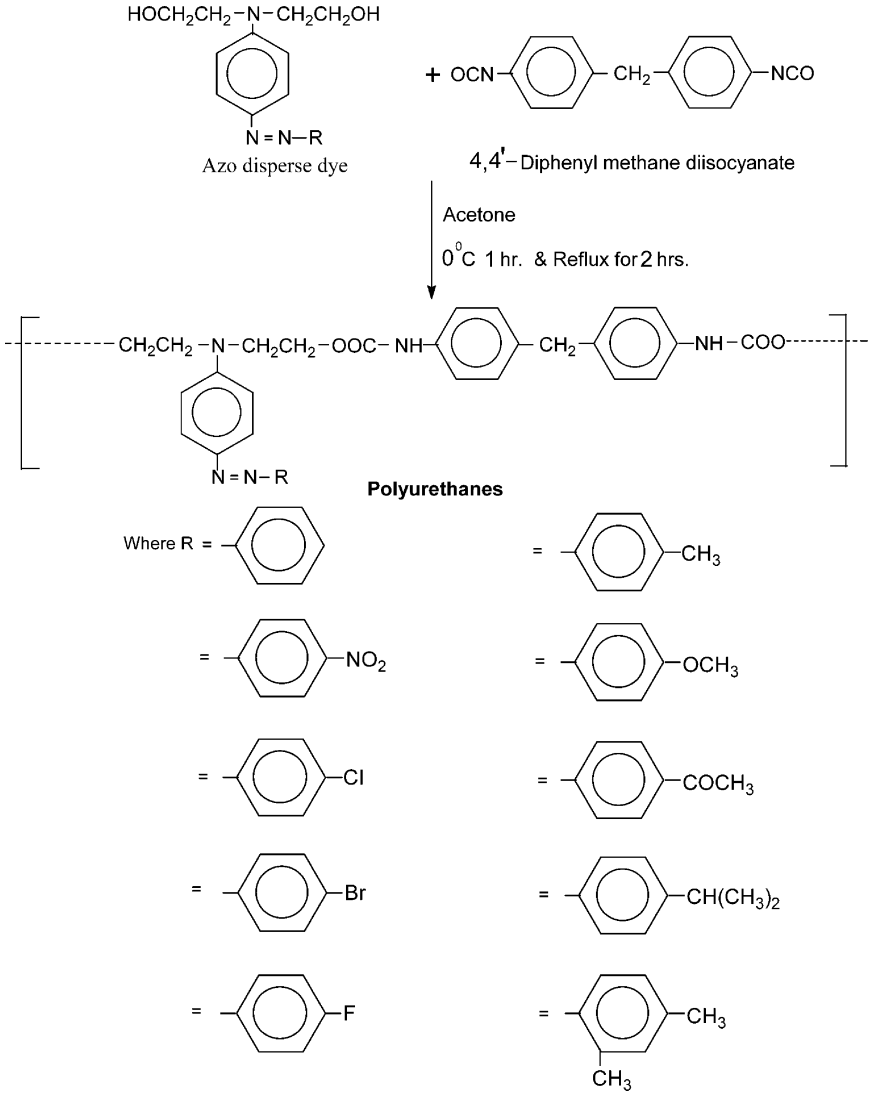
Synthesis of Colored Polyurethanes (PUs)

All the polyurethane based on azo disperse dyes was prepared in a similar manner. The general process is as follows.

To an ice cooled solution of azo disperse dye sample (0.01 moles) in dry acetone (50 ml) a solution of 4, 4′ -Diphenyl methane diisocyanate (0.01mole) in 50 ml dry acetone was added gradually with constant stirring. A colloidal suspension was immediately, formed which was then stirred at room temperature for an hour. The resultant suspension was refluxed ($\sim$60°C) for 2 h on a water bath. The resulting solid product was then filtered off and air-dried (95% yield).

Measurements

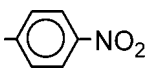
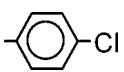
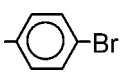
C,H,N contents of all polyurethanes samples were estimated by C,H,N,O, and S elemental analyzer, Carlo Erba, Italy. The IR spectra of the polymers were scanned in KBr pellets on Perkin Elemer 257 spectrophotometer, number average molecular weights ($\bar{M}n$) of PUs were estimated by non-aqueous conductometric titration. The titration was carried out in pyridine against standard sodium methoxide as



SCHEME 1

titrant. Digital conductometer, Toshniwal, India, was used for this purpose. The Mn values of all polymer samples were calculated following the method reported by one of the authors [10]. Thermogravimetric analyses for polymers were carried out on DuPont thermo balance in air at a heating rate of $10\,K\,min^{-1}$. The electrical

TABLE 1 Characterization of Polyurethanes (PUs)

PU sample	R=	Color of sample	Mole formula of repeating unit	Mol. wt. of repeating unit	Elemental analysis					
					% *C*		% *H*		% *N*	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
PU–1		Orange	$C_{31}H_{29}O_4N_5$	535	69.53	69.30	5.42	5.20	13.08	13.00
PU–2		Red	$C_{31}H_{28}O_6N_6$	580	64.13	64.00	4.82	4.60	14.48	14.30
PU–3		Yellow	$C_{31}H_{28}O_4N_5Cl$	569	65.37	65.10	4.92	4.80	12.30	12.10
PU–4		Dark Yellow	$C_{31}H_{28}O_4N_5Br$	614	60.58	60.10	4.56	4.40	11.40	11.20

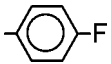
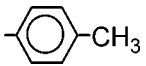
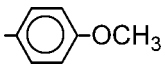
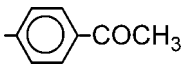
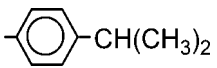
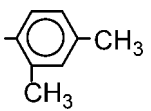
PU–5		Yellow	$C_{31}H_{28}O_4N_5F$	553	67.26	67.00	5.06	4.90	12.65	12.50
PU–6		Yellow Black	$C_{32}H_{31}O_4N_5$	549	69.94	69.80	5.64	5.40	12.75	12.60
PU–7		Brown	$C_{31}H_{31}O_5N_5$	565	67.96	67.70	5.48	5.30	12.38	12.10
PU–8		Dark Brown	$C_{33}O_{31}O_5N_5$	577	68.63	68.40	5.37	5.20	12.13	12.00
PU–9		Brown	$C_{34}H_{35}O_4N_5$	577	70.71	70.50	6.06	5.90	12.13	12.00
PU–10		Red	$C_{33}H_{34}O_4N_5$	564	70.21	70.10	6.02	5.80	12.41	12.30

TABLE 2 Number Average Molecular Weight (Mn) of PUs by Non-Aqueous Conductometric Titration

PU sample	M mol of NaOMe at y break (to neut. $-NH_2$group)	$Mn = \frac{100}{y \cdot 10^{-3}}$
PU–1	21	4760
PU–2	24	4160
PU–3	22	4540
PU–4	20	5000
PU–5	23	4350
PU–6	18	5560
PU–7	18	5560
PU–8	17	5880
PU–9	16	6250
PU–10	18	5560

conductivity of each of PUs sample was measured on pellets (1 cm diameter, 0.45 cm thickness) at room temperature ($30 \pm 1^{\circ}C$) using a Million Megohmmeter RM 160 MK IIA BPL, India. The preparation of the pellets and other details have been described in an earlier communication [11].

RESULTS AND DISCUSSION

The colored polyurethane (PU) formation was performed by a reaction of the $-OH$ groups of the dye moiety with $-NCO$ groups. All PUs shown in Scheme 1 are furnished in Table 1. They were found to be colored solid powders. They do not melt up to 250°C and are insoluble

TABLE 3 Electrical Conductivity of PUs

PU samples	Electrical conductivity (σ) at 303°K ($\Omega \cdot cm^{-1}$)
PU–1	4.6×10^{-8}
PU–2	2.3×10^{-10}
PU–3	5.8×10^{-9}
PU–4	7.0×10^{-9}
PU–5	1.2×10^{-9}
PU–6	4.3×10^{-7}
PU–7	3.2×10^{-7}
PU–8	2.3×10^{-7}
PU–9	8.4×10^{-7}
PU–10	9.8×10^{-7}

in common organic solvents. (C, H, N) contents (Table 1) of each of the PUs are consistent with the corresponding predicted structure (reaction scheme).

IR spectra (not shown) of all the PUs are identical in almost in all aspects and inspection reveals them to comprise important IR spectral features of urea and urethane linkages. The IR bands at $1680 - 1700\,cm^{-1}$ may be respectively due to urethane linkage [10]. The other IR spectral features due to aromatic and aliphatic segments appear at their expected positions.

As the produced PUs are insoluble in organic solvents, the colligative properties (i.e., viscosity, osmometry) have not been studied. Thus the number average molecular weight (Mn) of all the polymer sample has been estimated by non-aqueous conductometric titration of end $-OH$ group. The results of Mn values are furnished in Table 2.

TG thermograms (not shown) of all the PUs are identical in nature: all the PUs decomposed in one-step. They start their degradation about 200°C. The degradation start at 200°C is an indication of urethane groups. It is reported that polyurethanes start their degradation at 200°C due to decarboxylation [4,11].

The electrical conductivity data of all PUs, measured at room temperature, are presented in Table 3 and they are in the range of 2.3×10^{-10} to $2.3 \times 10^{-7}\,\Omega cm^{-1}$ depending upon the nature of each polymer. An examination of the results reveals that the produced PUs can be ranked as poor insulators. The application of PUs is under progress.

CONCLUSION

The present work is novel colored polyurethanes. These polymers are amorphous colored powders. They have good thermal stability. Looking to the properties of colored polyurethanes, the colors cannot bloom or bleed out of the articles.

REFERENCES

[1] Saunders, J. H. and Frisch, K. C. (1963). *Polyurethanes Chemistry and Technology* Wiley-Interscience, New York.
[2] Rigid Urethane Foam Technical Bulletin, Mobay Corp., Pittsburgh, Pa. (1981).
[3] Urethane Polyols for Flexible Foam Applications, Bulletin, Mobay Corp. Pittsburgh, Pa. (1981).
[4] Potter, T. A., Schmelzer, H. G., and Baker, R. D. *Prog. Org. Coat* **12**, 321 (1984).
[5] Tanaka, T., Yokoyana, T., and Yamuguchi, Y. Y. *J. Polym. Sci.*, part A-2, **6**, 2137 (1968).
[6] Naegeli, C. A. and Conrad, L. *Helv. Chem. Acta* **21**, 1127 (1938).

[7] Iwakura, Y., Hayashi, K., and Inagaki, K. *Makromol Chem.* **104**, 56 (1967).
[8] (1985). *Encyclopedia of Polymer Science and Engg.*, **13** (John Wiley and Sons, New York), p 212, 243.
[9] Desai, C. K. and Desai, K. R. *Iranian Polymer J.* **9**, 3 (2000).
[10] Patel, H. S., Patel, R. N., and Patel, S. R. *Angew. Makromol. Chem.* **99**, 125 (1981).
[11] Patel, K. B., Desai, K. R., and Patel, H. S. *Intern. J. Polymeric Mater.* **35**, 137 (1997).