Segmented Polyurethanes Using Fluorescein

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SYNOPSIS

Segmented Polyurethanes were prepared by chain extending the prepolymers based on poly(tetramethylene oxide)glycol and tolylene diisocyanate using fluorescein. The polymers were characterized using FTNMR and FTIR. Thermal stability of the polymers was studied using a thermogravimetric analyzer, and the glass transition temperature of the polymers was determined using a differential scanning calorimeter. Tensile strength and percentage of elongation of these segmented polyurethanes were evaluated using a Universal Testing Machine. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethanes are a very important class of block copolymers with wide ranging applications. The ability to tailor make these polymers by subtle modifications has led to voluminous work in this field. Segmented polyurethanes attracted ample interest both academically and commercially due to their superior properties.[1-4] Morphological study, effect of chain length,[5,6] and phase separation study using paramagnetic labels of polyurethanes[7] and the role of hydrogen bonding[8-10] have been studied in great detail. Fluorescein and their derivatives have been studied as color formers,[11] in clear magnetic imaging,[12] in UV photoresist patterning,[13] in polygluteraldehyde microspheres for immunological cell separation,[14] as aqueous space markers,[15] as xanthene poly dyes,[16] as cosmetics,[17] for extraction of metal traces,[18] etc. Several patents have appeared in the above mentioned areas. Morgan's detailed investigation on the use of phthalein, substituted phthaleins, and fluorescein as dihydroxy components for the preparation of polyesters threw open a new chapter on the vast field of high performance polymers using these components.[19] Introduction of hetero aromatic and aromatic moieties in polyurethanes considerably improves the properties of the polymers.[20] Aromatic dihydroxy compounds have been used to prepare segmented polyurethanes and have a wide application area.[21-23] In previous work from our labora-

tory phenolphthalein,[24] phthalins, and substituted phthalins[25,26] were used as chain extenders in the preparation of segmented polyurethanes. The polyurethanes synthesized from these rigid diol components (used as chain extenders) showed superior thermal and mechanical properties. In this article we present the investigations on segmented polyurethanes that are chain extended using fluorescein.

EXPERIMENTAL

Materials

Poly(tetramethylene oxide)glycol (PTMG, average molecular weights 1000, 2000, and 2900, Aldrich) was dried at 105°C in vacuum for 24 h before use. Tolylene diisocyanate (TDI, mixture of 80% 2,4 and 20% 2,6 isomers, Aldrich) and dibutyltin dilaurate (Aldrich) were used as received. Fluorescein (Loba Chemie, India) was recrystallized in acetone-ethanol (red crystals) and used. The solvent dimethylformamide (DMF, S.D. Fine Chem., India) was purified by standard distillation procedures and stored over 4-Å molecular sieves until use.

Synthesis of Chain Extended Polyurethanes

$PTMG_{1000}$ (10 g, 0.01 mol) was placed in a three-necked round bottomed flask and TDI (3.74 g, 0.02 mol) was added dropwise while maintaining the temperature at 60°C under nitrogen atmosphere.

The temperature was then increased to 90°C and the reaction was continued till the NCO content reached half the value as determined by dibutyl-amine titration. Then the temperature was reduced to 60°C and fluorescein (3.32 g, 0.01 mol, in 15 mL of DMF) was added followed by the catalyst dibutyltin dilaurate (0.01 g). The temperature of the reaction was then increased to 90°C and allowed to completed. The polymer was precipitated by pouring into a 10-fold excess of methanol and dried under vacuum at 35°C.

By a similar procedure polyurethanes of different compositions using polyols of different molecular weights were synthesized. The chemical composition and codes of the polymers are given in Table I. The reaction sequence is given in Scheme 1.
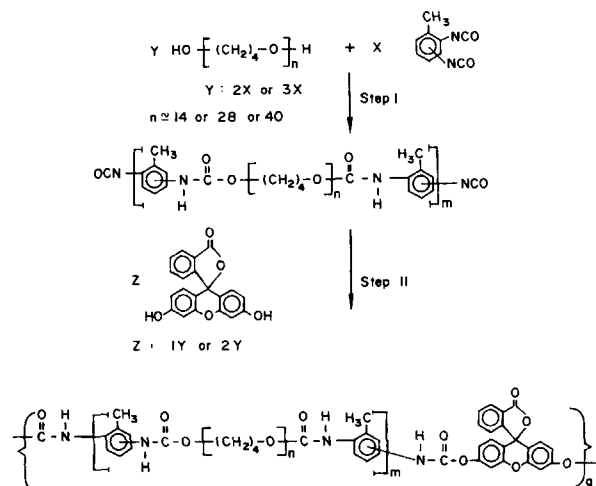
Scheme 1

RESULTS AND DISCUSSION

Molecular weight distribution of the polymers were evaluated using a Waters Associates gel permeation chromatograph with DMF (stabilized with 0.1% LiBr) as solvent at a flow rate of 1.0 mL/min. The columns used were micro-styragel of 10^6, 10^5, 10^4 and 10^3 Å size, calibrated with polystyrene standards. The molecular weight of polymers obtained from GPC are given in Table II. All the polymers showed appreciable molecular weights. This is consistent with our earlier work on phthalein and phthalin moieties[25,26] in which we observed that aromatic diols that were not sterically hindered yielded polymers with appreciable molecular weights. Also in sterically hindered systems like catechol and 3,4-dihydroxy cinnamic acid, molecular weights achieved were comparatively low (G. N. Mahesh, S. Ramesh, N. C. T. Gowthamram, and G. Radhakrishnan, Pers. commun.). From these data we can infer that for unhindered systems and where the distance between the two hydroxyl groups is more, higher molecular weights are achieved.

The broad molecular weight distribution observed is due to the polymer solvent interaction taking place when the polyurethane is dissolved in high polar

Table I Polymer Composition and Code

Composition	Code
PTMG$_{1000}$/2TDI/fluorescein	F$_1$
PTMG$_{2000}$/2TDI/fluorescein	F$_2$
PTMG$_{2900}$/2TDI/fluorescein	F$_3$
PTMG$_{1000}$/3TDI/2fluorescein	F$_4$

solvents. Many of these type of colored compounds' inherent difficulty is in dissolution in common solvents as observed by earlier reports.[27] Although there have been only very few reports of using these high polar solvents for GPC analysis, addition of a strong electrolyte minimized the abnormal distribution patterns observed in these systems.[28] However, we tried to rerun the sample under more vigorous inert conditions like nitrogen purging of the solvent to remove traces of oxygen and preventing the absorption of moisture to a very minimum level. We observed changes in the polymer elution curve giving reasonable polydispersity values.

Fourier transform nuclear magnetic resonance (FTNMR) were recorded on a Bruker MSLp 300-MHz spectrometer using DMSO-d_6 as solvent. The proton exchange technique was used to fix the —NH proton of the urethane linkages. In the synthesized polyurethane the soft segment part is the poly(tetramethylene oxide) (PTMG) and the hard segment part is the isocyanate and fluorescein units. The peak at 1.48 ppm (s) can be attributed to the methylene protons of the PTMG segment. The —O—CH$_2$— protons of the PTMG backbone were observed at 3.30 ppm.

The methyl protons of the hard segment of TDI are seen at 2.19 and 2.52 ppm. The protons of the aromatic hard segments namely TDI and fluorescein were observed at 6.53 (s), 6.71 (s), 6.82 (w), 7.24 (d), 7.67 (m), and 7.96 ppm (m). The peak at 4.05 ppm was due to —NH—O—CO—$\overline{CH}_2$ groups that link the hard and soft blocks. The urethane —NH protons of TDI resonate at 8.47, 8.23, and 9.13 ppm because it is a mixture of two isomers. From the ^{13}C spectrum of the polymers the methylene carbons of the PTMG segment absorbs at 26.04 ppm and the
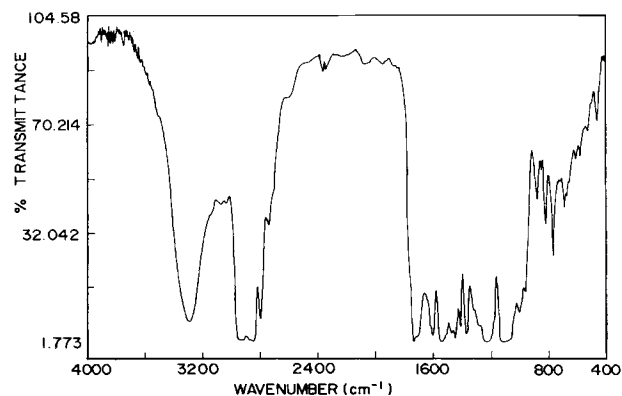
Table II Polymer Data

Composition	$\overline{M_n} \times 10^4$	$\overline{M_w} \times 10^5$	$\overline{M_w}/\overline{M_n}$	T_g (°C)	Tensile Strength at Break (N/mm^2)	Percentage Elongation at Break
F$_1$	9.71	7.68	7.91	−58	41.6	3400
F$_2$	4.41	1.40	3.17	−60	Soft	—
F$_3$	4.21	2.08	4.94	−64	Soft	—
F$_4$	2.06	0.29	1.42	−34	3.6	1760

—O—CH$_2$— at 69.71 ppm. The carbons of the aromatic rings are observed from 102 to 151 ppm. The carbonyl carbons of the urethane unit absorbs at 159 and 162 ppm.

Fourier transform infrared spectra (FTIR) of the polymers were recorded as a neat film using a Nicolet Impact 400 spectrometer. Polymer films for FTIR analysis were prepared by dissolving the purified samples in DMF, casting over a pool of mercury, and evaporation of the solvent at 60°C. The FTIR spectrum of F$_1$ is given in Figure 1. The stretching due to C—C (aromatic) is observed at 1601 cm^{-1} and the band due to C—N stretching and NH deformation (amide II band) is seen at 1532 cm^{-1}. The free carbonyl stretching of the urethane and that of the lactone of the fluorescein is observed at 1732 cm^{-1}. The hydrogen-bonded carbonyls are seen at 1698 cm^{-1}. Urethane NH stretching is seen at 3290 cm^{-1}. The C—O—C stretching from the PTMG segment is observed at 1110 cm^{-1}.

Thermogravimetric Analysis (TGA)

TGA was carried out using a Du Pont 951 thermogravimetric analyzer at a heating rate of 10°C/min under nitrogen atmosphere. The TGA curves of fluorescein and the polyurethanes are given in Figure

2. Fluorescein decomposes at about 350°C corresponding to 4% weight loss. All the polymers showed good thermal stability. The marginal initial weight loss up to about 160°C can be attributed to trapped solvent in the samples. The rigid diol component in the polymers seemed to induce much higher thermal stability to the polymers. F$_2$ and F$_4$ show a double stage decomposition pattern. The second stage decomposition can be attributed to the decomposition of a combination of chemical segments in the polymer chain. The urethane linkages of aromatic diol and aromatic diisocyanate decompose at about 180°C. The absence of significant weight loss here can be due to the fact that the TGA runs were not performed under isothermal conditions but at a steady heating rate. Also the products formed in the decomposition are not volatile enough to be carried by the nitrogen carrier gas.

DSC Analysis

The DSC study was performed on a Du Pont 910 instrument at heating rate of 10°C/min under nitrogen atmosphere (Fig. 3). For each run the amount of sample taken was 10 ± 0.2 mg. The glass transition temperature (T_g) of the polyurethanes mainly

Figure 1 FTIR spectrum of F$_1$.
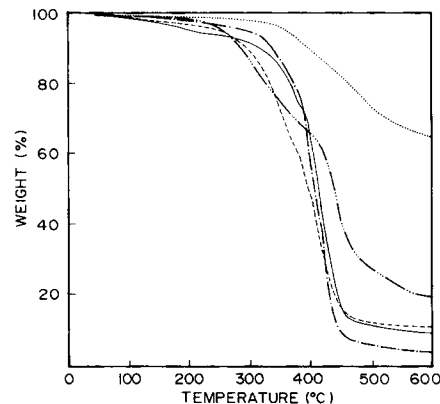
Figure 2 TGA curves of (· · ·) fluorescein, (- - -) F$_1$, (—) F$_2$, (- · -) F$_3$, and (- · · · -) F$_4$.
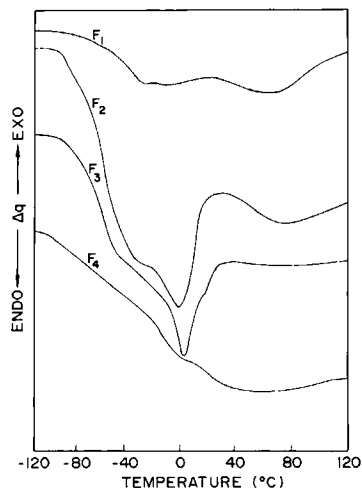
Figure 3 DSC thermograms of F_1, F_2, F_3, and F_4.

depends on the soft segment part. All the polymers had their T_g below room temperatures, which is the characteristic of the soft segments used. When we compare polyurethane F_1 and F_4 for the same polyol used, F_4 had higher T_g. This is due to the good mixing of the hard segments in the soft segment so that efficient phase separation between the two segments is lowered. This is also seen from the broad nature of transition for F_4. The T_g of F_2 and F_3 is lower than F_1 due to the nature of the polyol segments. The endothermic transitions observed after the T_g for these samples is due to the crystalline melting of $PTMG_{2000}$ and $PTMG_{2900}$ units.

Mechanical Properties

Mechanical properties of the polymer were evaluated using an Instron Universal Testing Machine Model 4501 at a crosshead speed of 50 mm/min. The samples for tensile testing were prepared by solution casting the polymers in DMF medium into silicon troughs and by slow evaporation of the solvent at 60°C. The specimens were cut into dumbbell shape of 2.1- length and 0.4-cm breadth. Three specimens were subjected to testing for each sample. The ultimate tensile strength and percent elongation of $PTMG_{1000}$ based polymers showed much superior behavior. This can be attributed to stress induced crystallization in case of $PTMG_{1000}$ based polymers. Here the ratio of soft segment and hard segment (inclusive of urethane linkage and rigid diol component) form the balance to give superior properties. Further, increased molecular weight of the polymer plays a very important role in the mechanical properties and is evident from the fact that although F_1

and F_4 contain the same components (in different mole ratios), F_1 shows much better properties.

CONCLUSION

The introduction of a rigid aromatic component in polyurethanes enhances the properties of the polymers. All the polyurethanes could be cast as films, but the films based on $PTMG_{2000}$ and $PTMG_{2900}$ were very soft. $PTMG_{1000}$ based polymer films had very good gloss and flexibility. The properties of these films can be further improved by preventing voids caused by unequal solvent evaporation. To further harness the potential of these high performance materials, efforts are being made to incorporate ionic moieties and metal ions.

REFERENCES

1. S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **10**, 1837 (1966).
2. M. V. Pandya, D. D. Deshpande, D. G. Hundiwale, and V. R. Kapadia, *J. Macromol. Sci. Chem.*, **A24**, 527 (1987).
3. H. Nakamura, T. Takata, and T. Endo, *Macromolecues*, **23**, 3032 (1990).
4. S. Ramesh, P. Rajalingam, and G. Radhakrishnan, *Polym. Int.* **25**, 253 (1991).
5. A. L. Chang, R. M. Briber, E. C. Thomas, R. J. Zdrahala, and F. E. Critchfield, *Polymer*, **23**, 1060 (1982).
6. J. Blackwell, M. R. Nagarajan, and T. B. Hoitink, *Polymer*, **23**, 950 (1982).
7. W. P. Chin and S. Schlick, *Polymer*, **31**, 308 (1990).
8. M. M. Coleman, D. J. Skrovanek, J. Hu, and P. C. Painter, *Macromolecules*, **21**, 59 (1988).
9. M. M. Coleman, D. J. Skrovanek, and P. C. Painter, *Macromolecules*, **19**, 2149 (1986).
10. M. M. Coleman, D. J. Skrovanek, and P. C. Painter, *Makromol. Chem. Macromol. Symp.*, **5**, 21 (1986).
11. W. Bernhard Eur. Pat. Appl. EP 373,104 (Cl.C07D493/10) (1990) (to Ciba–Geigy AG).
12. T. Kamitaki, Y. Sato, and I. Osaki, Jpn. Pat. 2,293,863 (90,293,863) (CL.G0349/09) (1990) (to Cannon, K.K.).
13. M. Endo, M. Sasaka, N. Nomura, Jpn. Pat 2,118,660 (90,118,660) (to Matsushita Electric Industrial Co., Ltd.) (CL.GO3F7/20) (1990) (to Matsushita Electric Industrial Co., Ltd.).
14. A. Rem Baun and S. Margel U.S. Pat. 4,267,235 (CL428-407→2B5/16) (1981) (to California Institute of Technol.)

15. F. C. Szoka, Jr., K. Jacobson, and D. Papahadjopou-lous, *Bio. Chim. Biophys. Acta,* **551**, 295 (1979).
16. C. E. Carraher, Jr., R. A. Schwarz, J. A. Schroeder, M. Schwarz, and H. M. Molloy, *Org. Coat. Plast. Chem.,* **43,** 798 (1980).
17. M. Guillon, J. Mondet, C. Papantoniou, and C. Van den bossche, Fr. Pat. 2,480,770 (CL.CO 9B69/10) (1981) (to Oreal S. A.)
18. K. P. Stolyarov and V. V. Friyulina, *Probl. Sovrem. Analit. Khimi, Leningrad,* **3,** 65 (1981) (in Russian).
19. P. W. Morgan, *J. Polym. Sci., Polym. Chem. Ed.,* **2,** 437 (1964).
20. C. X. Lu, Y. Yang, C. Xiao, and A. Ji, *J. Polym. Sci., Polym. Chem. Ed.,* **25,** 3267 (1987).
21. F. Papadimitrakopoulos, S. L. Hsu, and W. J. Mack-night, *Macromolecules,* **25,** 4671 (1992).
22. F. Papadimitrakopoulos, E. Sawa, and W. J. Mack-night, *Macromolecules,* **25,** 4682 (1992).
23. K. R. Haridas and G. Radhakrishnan, *J. Polym. Sci., Polym. Chem.,* **33,** 901 (1995).
24. H. Rajan, P. Rajalingam, and G. Radhakrishnan, *J. Appl. Polym. Sci.,* **48,** 2095 (1993).
25. S. Ramesh and G. Radhakrishnan, *Polymer* **35,** 3107 (1994).
26. S. Ramesh., *Ph.D. Thesis,* University of Madras, Madras, India, 1994.
27. J. T. Guthrie, *Rev. Prog. Coloration,* **20,** 40 (1990).
28. T. Y. T. Chui, M. H. George, and J. A. Barrie, *Polymer,* **33,** 5254 (1992).