# Synthesis and properties of monodisperse hydroxy-terminated oligomers of 1,4-butanediol and 2,4-toluene diisocyanate

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The synthesis of monodisperse hard segments containg 2,4-TDI and 1,4-butanediol by a simple technique is described. High purity material is obtained in good yield. The structures of these hard segments are confirmed by proton n.m.r., $^{13}$C n.m.r., and i.r. Glass transition temperatures and melting temperatures are reported. The $T_g$'s of the hard segments are inversely proportional to the reciprocal of their molecular weights. The $T_m$'s show an odd–even effect relative to the number of 2,4-TDI units in the hard segment.

**(Keywords: monodisperse; blocking-deblocking; excess endcapping; 2,4-toluene diisocyanate; 1,4-butanediol)**

## INTRODUCTION

Segmented polyurethanes are alternating block copolymers containing soft and hard segments of various lengths. Soft segments are usually low glass transition temperature polyesters or polyethers with molecular weights ranging from 1000 to 3000. Hard segments, being glassy or partially crystalline at ambient conditions, are generally formed from the extension of a diisocyanate such as 2,4-toluene diisocyanate (2,4-TDI) or 4,4′-diphenylmethane diisocyanate (MDI) with a low molecular weight diol such as 1,4-butanediol (BDL).

The concept of phase segregation[1,2], with the hard segment domains dispersed in a rubbery matrix, has been accepted as the explanation for the thermoplastic elastomer properties of the segmented polyurethanes.

By changing the components and their relative ratios, a variety of segmented polyurethanes with different properties can be obtained. The properties depend largely on the glass transition temperature ($T_g$) or melting temperature ($T_m$) of both the soft and the hard segments; the domain size and shape, the crystallinity, and the internal organization of the hard segments; and the compatibility between the soft and the hard segments. These factors are further related to the hard segment length and its distribution. The various segment lengths of regular segmented polyurethanes are mostly due to the differences in reactivities; polymerization conditions such as temperature, catalyst, mixing and solvent; and polymerization methods, either the one-step or the two-step process. Even in the randomly copolymerized segmented polyurethanes a distribution of hard segments lenths is inevitable[3].

Techniques such as nuclear magnetic resonance (n.m.r.) and depolymerization have been used to study the average sequence length of the hard segments in a limited number of polyurethanes. Suzuki *et al.*[4] have obtained the average hard segment length of several polyester based polyurethanes by proton n.m.r. using several model compounds. Suzuki and Ono[5] have depolymerized a poly(ether)–urethane elastomer with perchloric acid. The number average molecular weight of the urea segment was determined by elemental analysis and by volumetric analysis. Nevertheless, the depolymerization technique can only be applied to very few polyurethanes due to the difficulty in breaking a specific bond. Since it is difficult to obtain the distribution of the segments, most of the structure–property studies can only relate morphologies and properties to the hard segment content instead of the actual segmental distribution. An alternate route to studying the structure–property relationships is to use a series of polyurethanes with controlled hard segment lengths. These polymers should provide important information about the domain sizes and shapes, mechanical properties, thermal properties and transport phenomena as a function of the hard segment length.

Polyurethanes containing monodisperse hard segments can be prepared by condensation or addition polymerization from polyols and monodisperse hard segments, both with suitable end group capable of forming urethane linkages. In general, there are two basic methods, namely the blocking–deblocking process and the excess endcapping process for the preparation of monodisperse hard segments. Harrel[6] studied the poly(tetramethylene ether glycol) (PTMEG)–piperazine–BDL system where hydrogen bonding did not exist. He prepared hard segments, up to four units, by connecting piperazine and butanediol with phosgene. Amino-terminated hard segments were formed by the blocking–deblocking process using carbobenzyloxy blocking groups. Kern *et al.*[7] prepared hexamethylene diisocyanate

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(HMDI)–BDL hard segments by an endcapping process with a large excess of endcapping materials. Recently, monodisperse MDI–BDI hard segments have been studied more intensively. Camberlin *et al.*[8] prepared alkyl-terminated hard segments in order to study the chain end effects on the melting properties. Eisenbach and Gunter[9] and Macosko *et al.*[10] have successfully prepared monodisperse hard segments of the MDI–BDL system with hydroxyl end groups capable of forming segmented polyurethanes.

Our laboratory has studied[11] a completely amorphous polyurethane system containing polybutadiene soft segments and 2,4-TDI–BDL segments. The hard segments, unlike those of the MDI–BDL system, do not crystallize. Therefore, the effect of hydrogen bonding on properties can be determined more esily. In these bulk polymerized polyurethanes, two hard segment $T_g$'s were observed. This is in accordance with the observations by Schneider *et al.*[12], although the hydroxy functionality of the polybutadienes was different (1.97 vs. 2.3). Apparently the existence of two hard segment $T_g$'s does not arise from chemical crosslinking. Later it was suggested[13] that the reactant incompatibility may cause a hard segment bimodal distribution and this is responsible for the two hard segment $T_g$'s. A model of phase segregation was proposed by Chen *et al.*[14] on the same system. However, the compatibility of long and short hard segments remains unknown. It is one of our future goals to answer this question by blending segmented polyurethanes containing monodisperse hard segments of different lengths.

In this study, monodisperse hard segments based on 2,4-TDI and BDL are prepared and characterized. In a forthcoming paper, we will discuss the properties of the segmented polyurethanes made from these hard segments and various types of soft segments.

## METHOD

Dimers are prepared by endcapping 2,4-TDI with a large excess of BDL. Crude dimers are purified by fractional precipitation. Trimers and higher oligomers are prepared by a simple blocking–deblocking process taking advantage of the different reactivities of the isocyanate groups in 2,4-TDI and the characteristics of an oxime blocking group. It is well known[15] that the two isocyanate groups in 2,4-TDI are different in reactivities: para-isocyanate reacts about 10 times faster than ortho-isocyanate towards alcohols. This means the para-isocyanate group can be blocked while the ortho-isocyanate group remains free. Such a partially blocked 2,4-TDI enables us to incorporate a glycol into the molecule without using excess endcapping material. Oximes have been known[16] as blocking agents for preparing one-component blocked urethanes where the isocyanate groups are re-generated by heating. Guise *et al.*[17] have shown that oximes could be removed within 15 minutes at 100°C in such blocked polyurethane. In this study, acetone oxime is chosen because its partially blocked 2,4-TDI adduct precipitates from the reaction medium, toluene, thus eliminating the need for purification. In addition, acetone oxime is soluble in water, which facilitates its removal after deblocking. Since acetone oxime is deblocked at elevated temperatures, the re-generated isocyanate group can react with added butanediol to obtain the desired hard segments. Hard segments are hydroxy-terminated which avoids side reactions during purification.

## MATERIALS AND INSTRUMENTS

Both 1,4-butanediol (Aldrich Chemical) and 2,4-toluene diisocyanate (Sigma Chemical) were purified by vacuum distillation. Anhydrous toluene (Aldrich Chemical) and dibutyltin dilaurate (Alfa Chemical) were used as received. Acetone oxime (Aldrich Chemical) was distilled before use. HPLC grade dimethyl formamide (Fisher Scientific) was refluxed and distilled three times with TDI, $CaH_2$ and TDI, respectively.

A Varian-T60 was used for proton n.m.r. using 100% deuterated dimethyl sulphoxide (DMSO) as a solvent for hard segments. Deuterated chloroform was used to analyse the adduct of 2,4-TDI and acetone oxime. $^{13}C$ n.m.r. spectra were obtained with a Varian-CFT-20 using deuterated DMSO as a solvent. Infra-red spectra were taken from a Perkin-Elmer 283 Infra-red Spectrometer using KBr pellets. Differential scanning calorimetry (d.s.c.) traces were obtained with a Perkin-Elmer DSC-2 equipped with a data station. Hard segments of 5 to 10 mg weight were used. The heating rate was 10°C/min and the cooling rate was either 320°C/min or 10°C/min. High performance liquid chromatograph (h.p.l.c.) results were obtained with a Perkin-Elmer Series 2 liquid chromatograph equipped with a data station using a $\mu$-porasil silica gel column (Waters Associates) under the conditions: (THF as a solvent, u.v. detector at 254 nm, flow rate 1 ml/min, and room temperature). Thin layer chromatograph (t.l.c.) results were obtained from a 20 cm × 20 cm silica plate (Fisher Scientific) using THF/hexane (60/40, V/V) solvent system.

## SYNTHESIS

*Table 1* shows the scheme for the synthesis of hard segments B(TB)n where B represents 1,4-butanediol and T represents 2,4-toluene diisocyanate. The adduct of actone oxime and 2,4-TDI is abbreviated as AT.

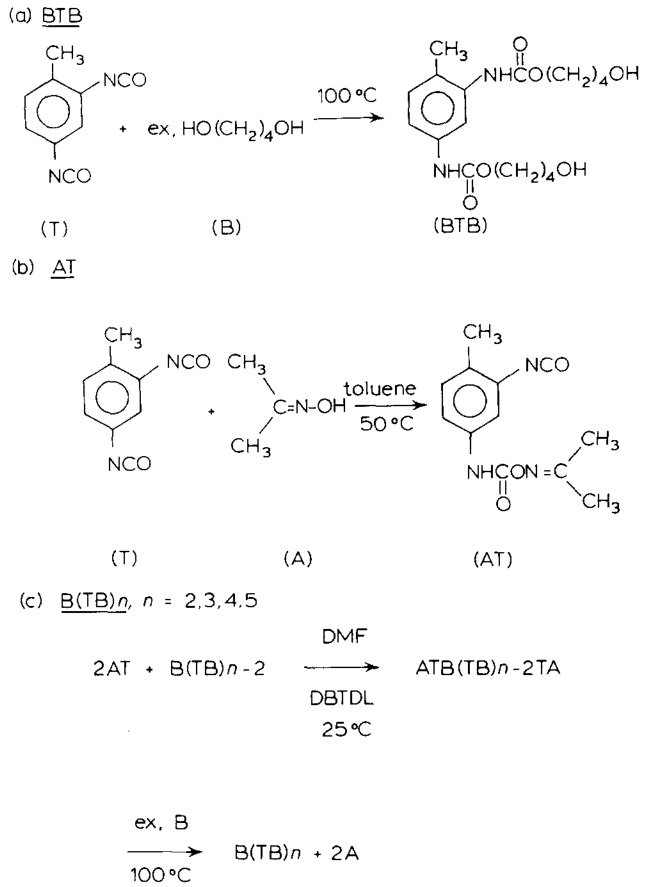
(a) BTB: 2,4-TDI (0.25 mole, 43.5 g) was added dropwise to stirred BDL (5 moles, 450 g) in a 1000 ml 3-neck flask at 100°C. The reaction was allowed to proceed for an additional two hours after complete addition of 2,4-TDI. The excess butanediol was removed completely by vacuum distillation. The residue was dissolved in methanol (2000 ml). Water was added until the solution became cloudy. The precipitate formed overnight was collected and analysed by h.p.l.c. or t.l.c. until the pure dimer was finally collected. The yield was 40 g (45%).

(b) AT: Acetone oxime (0.7 mole, 51 g) dissolved in dry toluene (150 ml) was added dropwise to 2,4-TDI (0.7 mole, 123 g) at 50°C in a 3-neck 500 ml flask equipped with a nitrogen inlet, a drying tube and a mechanical stirrer. Reaction was allowed to proceed for an additional two hours before cooling to room temperature. The white precipitate formed upon cooling was collected and washed with portions of 500 ml of toluene. Toluene was removed *in vacuo* at 50°C. The yield was 122 g (70%).

(c) B(TB)*n*, $n=2$, 3, 4, 5: Since the procedures are generally the same for all oligomers, the detail for the trimer synthesis only are described.

AT(0.2 mole, 49.4 g) BDL (0.1 mole, 9 g) and DMF (300 ml) were placed in a 1000 ml 3-neck flask equipped with a nitrogen inlet, a condenser, and a drying tube. DBTDL catalyst (0.01 g) was added and the reactants were stirred for one hour at room temperature. A slight excess of AT might be needed since the AT used was not

**Table 1** Synthesis of hydroxy-terminated hard segments of 1,4-butanediol and 2,4-TDI



Key: B, 1,4-butanediol; T, 2,4-TDI; A, acetone oxime; AT, adduct of 2,4-TDI and acetone oxime; DBTDL, dibutyltin dilaurate

pure. After the reaction was completed, as evidenced by the i.r. spectrum, BDL (2 moles, 180 g) was added to the reaction mixture and the temperature raised and kept at 100°C with stirring for two hours. The solution was allowed to cool to room temperature and poured into water (2000 ml) containing $CaCl_2$ (2 g). The precipitate was collected and washed several times with water. The crude product was dissolved in methanol (2000 ml) and water added until cloudy. The precipitate was collected overnight. This fractional precipitation procedure was continued until the desired fraction of the hard segments as analysed by t.l.c. or h.p.l.c. was obtained. The yield was 46 g (75%).

### *Characterization*

The structures of the adduct of 2,4-TDI and acetone oxime (AT) were confirmed by proton n.m.r. (*Figure 1*). Two types of methyl groups at 2.23 ppm and 2.07 ppm are observed. They are assigned to the methyl group attached to the benzene ring and the acetone oxime methyl group, respectively. The proton ratio is slightly lower than the expected ratio of 1:2. The deviation is due to the reaction between the ortho-isocyanate group and the acetone oxime. The amount of the side product formed can be calculated semi-quantitatively from the actual proton ratios. Our results show a purity of more than 90% for the crude product. No attempt has been made to further purify this material. The singlet appearing at 8.06 ppm is assigned to the proton on the para-substituted urethane linkage. The ortho-urethane linkage, if it exists, should appear at 7.60 ppm as evidenced in one of our di-substituted samples. This peak can also be used as an indication of di-substitution. The peaks at 6.97 ppm and 7.17 ppm correspond to the aromatic protons.

The purity of the hard segments is analysed by high performance liquid chromatography (h.p.l.c.) (*Figure 2*). The hard segments of various lengths show different retention times. U.v. absorptivity of each hard segment is found to be approximately the same. We may, therefore, conclude that the purity of the hard segments is better than 90% according to the h.p.l.c. traces. The purity is also apparent from the good agreement between calculated and observed values of the chemical compositions (*Table 2*). Tolerance limit of the elemental analysis is ±0.3%.

The structure of the hard segments is confirmed by proton n.m.r. *Figure 3* shows the n.m.r. spectrum of the dimer, BTB. The chemical shift assignments are listed in *Table 2*. The other hard segments show nearly the same chemical shifts but the proton ratios are different (*Table 3*). The triplet appearing at 4.33 ppm is assigned to the hydroxyl group adjacent to the methylene group (3.37 ppm). The intensities of these two peaks relative to the other peaks decrease as the hard segment length increases due to the lower content of $CH_2OH$ groups in the longer hard segments. The spectrum of the hexamer, $B(TB)_5$, is shown in *Figure 4* for comparison. The proton

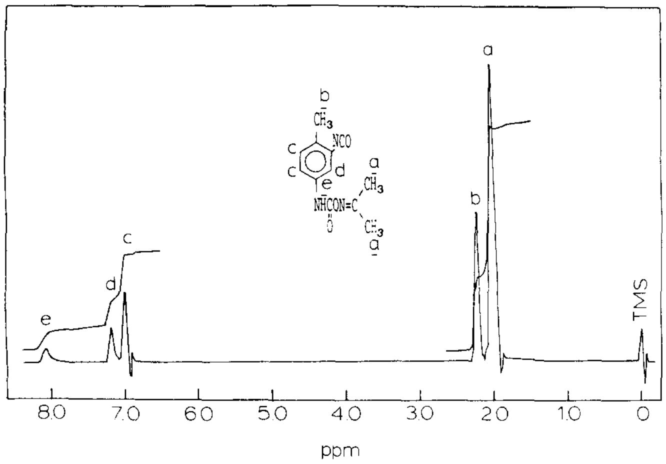


**Figure 1** Proton n.m.r. spectrum of the para-substituted adduct of 2,4-TDI and acetone oxime

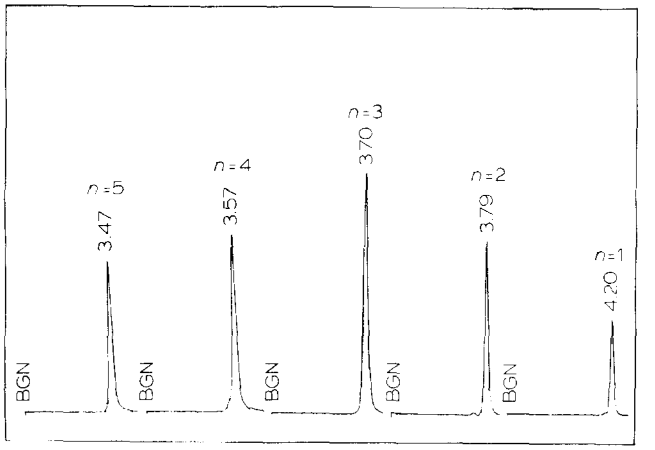


**Figure 2** H.p.l.c. traces of hard segments B(TB)$n$; $n$ = 1, 2, 3, 4, 5

**Table 2** Elemental analysis of hard segments

| | Calculated | | | | Found | | | |
|---|---|---|---|---|---|---|---|---|
| Oligomers | C | H | N | O | C | H | N | O* |
| Dimer | 57.63 | 7.34 | 7.91 | 27.12 | 57.47 | 7.46 | 7.87 | 27.20 |
| Trimer | 58.25 | 6.80 | 9.06 | 25.89 | 57.69 | 6.84 | 9.05 | 26.42 |
| Tetramer | 58.50 | 6.58 | 9.52 | 25.40 | 58.26 | 6.68 | 9.43 | 25.63 |
| Pentamer | 58.64 | 6.46 | 9.77 | 25.13 | 58.52 | 6.40 | 9.95 | 25.13 |
| Hexamer | 58.72 | 6.38 | 9.93 | 24.96 | 58.44 | 6.52 | 9.93 | 25.11 |

* by difference

**Table 3** Calculated and observed proton ratios and chemical shifts of hard segments

| Peak | | Dimer | Trimer | Tetramer | Pentamer | Hexamer | Chemical shift (ppm) |
|---|---|---|---|---|---|---|---|
| a | $(CH_2)_2$ | 8(8)* | 12(12) | 16(16) | 20(20) | 24(24) | 1.46 |
| b | $CH_3$ | 3(3) | 6(6) | 9(9) | 12(12) | 15(15) | 2.13 |
| c | $\underline{CH_2}OH$ | 4(4) | 4(4) | 4(4) | 4(4) | 4(4) | 3.37 |
| d | $COOCH_2$ | 4(4) | 8(8) | 12(12) | 16(16) | 20(20) | 4.05 |
| e | $CH_2\underline{OH}$ | 2(2) | 2(2) | 2(2) | 2(2) | 2(2) | 4.33 |
| f, g | phenyl | 3(3) | 6(6) | 9(9) | 12(12) | 15(15) | 6.98; 7.40 |
| h, i | NH | 2(1.7) | 4(3.4) | 6(5.4) | 8(7.3) | 10(8.4) | 8.51; 9.25 |

* Observed values

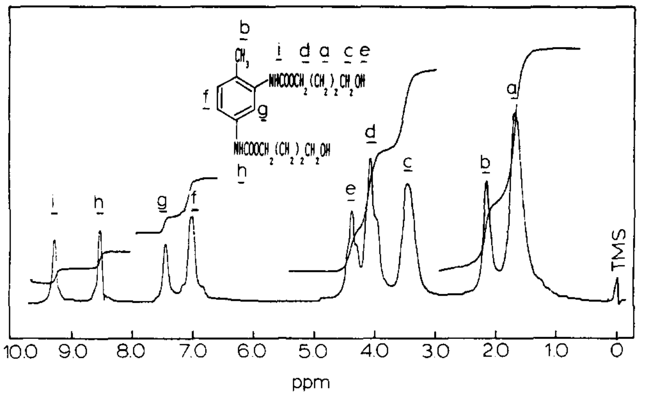


**Figure 3** Proton n.m.r. spectrum and the assignments of the dimer, BTB

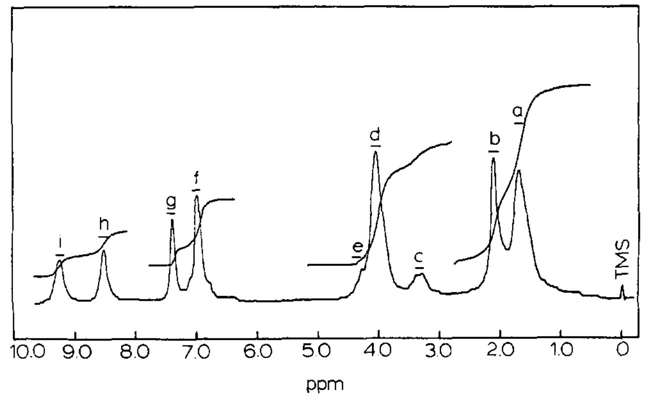


**Figure 4** Proton n.m.r. spectrum of the hexamer, $B(TB)_5$

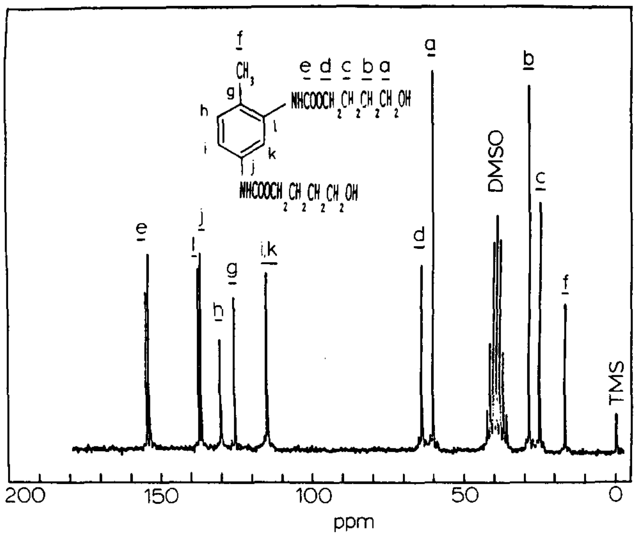


**Figure 5** $^{13}C$ n.m.r. spectrum and the assignments of the dimer

ratios of each group are generally in good agreement with the calculated values. The lower value of the proton of the urethane linkage (NHCOO) is possibly due to the proton–deuterium exchange with the solvent, deuterated dimethyl sulphoxide. The hydroxyl group, however, shows complete proton-deuterium exchange with solvents such as deuterated acetone and methanol.

The structures of the hard segments are further supported by $^{13}C$ n.m.r. *Figure 5* shows the $^{13}C$ n.m.r. spectrum of the dimer. All the peaks are identified using a variety of model compounds. The results are shown in *Table 4*. Again, the other hard segments show nearly the same chemical shifts but with different intensities. The intensities of peaks a and b decrease drastically as the hard segment length increases (*Figure 6*). It should be noted that the two methylene groups represented by peaks b and c are inseparable in proton n.m.r. but separable in $^{13}C$ n.m.r. The high intensity of peak c in the hexamer is due to the high content of the two internal methylene groups. The intensities of the other peaks change only slightly as expected.

The infra-red spectrum of the dimer is shown in *Figure 7*. The free NH stretching appears at 3460 $cm^{-1}$, the hydrogen bonded NH stretching at 3330 $cm^{-1}$, and the carbonyl bgroup at 1700 $cm^{-1}$.[18] The OH absorption cannot be separated clearly from bonded NH stretching.

**Table 4** Calculated and observed carbon chemical shifts of hard segments

| | Calculated* | Observed |
|---|---|---|
| a | 61.8 | 60.38 |
| b | 28.1 | 28.89 |
| c | 24.5 | 25.38 |
| d | 64.1 | 64.09 |
| e | 154.0 | 154.37 |
| f | 17.1 | 17.07 |
| g† | 125.66 | 125.55 |
| h† | 130.29 | 130.10 |
| i† | 114.95 | 114.96 |
| j† | 136.54 | 136.46 |
| k† | 114.95 | 114.96 |
| l† | 137.31 | 137.23 |

* Based on the following model compounds: hexane, 1-hexanol, 1,6-hexanediol, carbamate of phenyl isocyanate and 1-hexanol, and butane
† Based on the methyl dicarbamate of 2,4-TDI

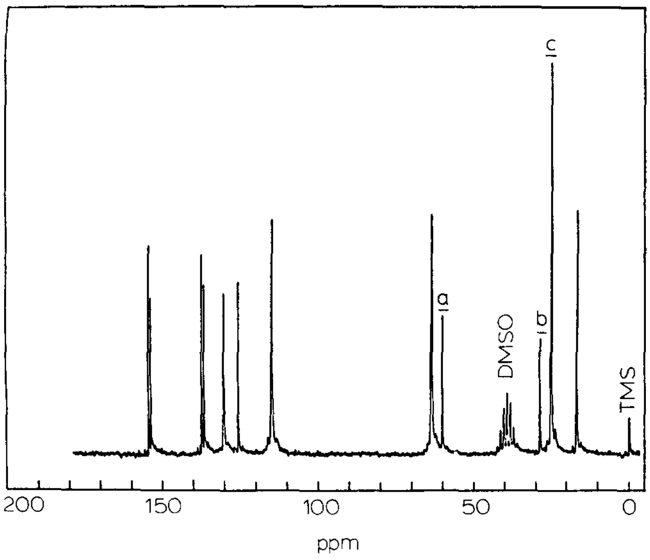


**Figure 6** $^{13}C$ n.m.r. spectrum of the hexamer

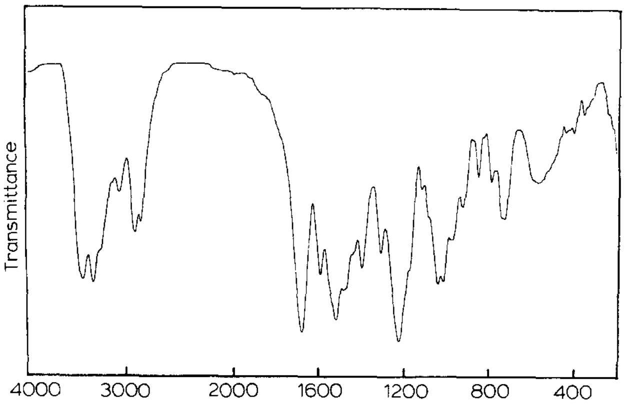


**Figure 7** Infra-red spectrum of the dimer

The other hard segments show similar spectra with changes in intensities.

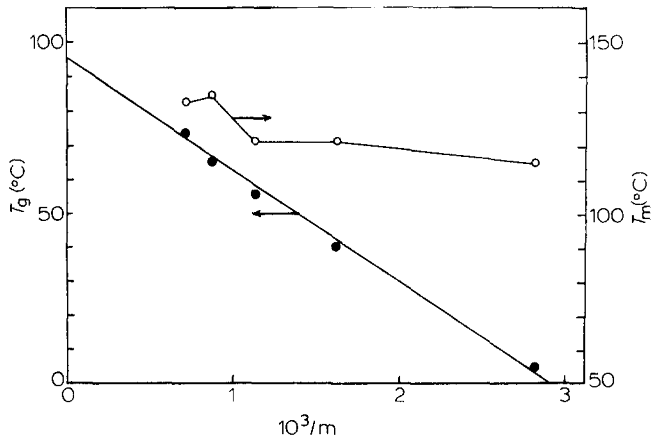


**Figure 8** Molecular weight dependence of $T_g$ and odd–even effect of $T_m$ in hard segments

**Table 5** Thermal properties of hard segments

| | $T_m$(°C) | $T_g$†(°C) |
|---|---|---|
| Dimer | 115 | 9 |
| Trimer | 122 | 45 |
| Tetramer | 120 | 61 |
| Pentamer | 136 | 70 |
| Hexamer | 133 | 78 |

* Peak temperature
† Midpoint

Melting points ($T_m$'s) and glass transition temperatures, ($T_g$'s), as functions of the hard segment length are shown in *Figure 8*. The hard segments, after drying at 100°C for 24 h, show a melting point during the first run. The quenched samples (320°C/min or 10°C/min cooling rate), on the other hand, show only glass transition temperatures. $T_g$ and $T_m$ values are collected in *Table 5*. The hard segment $T_g$'s are inversely proportional to the reciprocal of the molecular weight. Such a trend was also found in solution polymerized segmented polyurethanes containing the same type of hard segments and a butadiene soft segment[19]. The $T_m$'s of the hard segments show an odd–even effect relative to the number of TDI units. Even-numbered hard segments show higher melting temperatures than the neighbouring odd-numbered hard segments. Such behaviour is often found in polyamides or polyesters.

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