

Effects on Properties of Varying the *cis/trans* Isomer Distribution in Polyurethane Elastomers Made with 1,4-Cyclohexane Diisocyanate

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SYNOPSIS

Polyurethane elastomers have been made using 1,4-cyclohexane diisocyanate (CHDI), 1,4-butanediol (BDO) and a 2000 M_n polyether diol soft segment. The *cis/trans* isomer distribution of the CHDI was varied between 23% and 100% *trans*. This variation in isomer distribution had significant effects on the polyurethane's thermal and physical properties.

Decreasing the *trans* CHDI content gives polyurethanes with lower hardness, lower thermal stability, higher Coefficient of Linear Thermal Expansion (C.L.T.E.) values and decreased modulus values. Morphology studies showed good phase separation between the hard and soft segment blocks as well as a block copolymer morphology between the *cis* and *trans* CHDI/BDO blocks in the hard segment. The polyurethanes made were compared to polyurethanes made with MDI and H_{12} MDI, the leading aromatic and aliphatic diisocyanates respectively.

INTRODUCTION

Several papers have been published¹⁻⁵ concerning the use of 1,4-cyclohexane diisocyanate (CHDI) as an aliphatic monomer for use in high performance polyurethane elastomers. These studies have primarily dealt with the use of 100% *trans* CHDI. In our experiments, the *cis/trans* isomer distribution was varied between 23% and 100% *trans* and the effects this had on polymer properties and morphology were studied.

The first part of our two phase study involved using a model hard segment approach in which polymers were made by reacting CHDI with 1,4-butanediol (BDO) at a 1 : 1 stoichiometry via a solution polymerization technique. These linear polymers were then analyzed by differential scanning calorimetry (DSC) to determine what effect varying the isomer distribution had on the polymer's thermal properties.

The second phase of our work was done using linear polyurethane elastomers made with a CHDI/

BDO hard segment and a 2000 M_n polyether diol soft segment (Voranol™ 5287). These polymers, made at a hard segment concentration of 35 wt %, showed dramatic changes in the flexural storage moduli (E') as the isomer distribution of the CHDI was varied between 23% and 100% *trans*. These polymers were also compared to those made with diphenylmethane diisocyanate (MDI) and dicyclohexylmethane diisocyanate (H_{12} MDI), the leading aromatic and aliphatic diisocyanates respectively. All plaques were characterized by dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), and thermogravimetric analysis (TGA). Wide angle X-ray analysis (WAXS) was also used to determine percent crystallinity of the polymers.

EXPERIMENTAL

Starting Materials

1. 100% *trans*-1,4-Cyclohexane diisocyanate was obtained from Akzo Chemie America (Elate™ 166). The material was purified by

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Table I CHDI Isomer Distribution in Model Hard Segments

Sample	CHDI Isomer Distribution
I	20% <i>trans</i> /80% <i>cis</i>
II	30% <i>trans</i> /70% <i>cis</i>
III	40% <i>trans</i> /60% <i>cis</i>
IV	50% <i>trans</i> /50% <i>cis</i>
V	70% <i>trans</i> /30% <i>cis</i>
VI	100% <i>trans</i>

vacuum distillation prior to use (145°C at 5 mmHg).

- 23% *trans*-1,4-Cyclohexane diisocyanate was obtained as follows: *p*-phenylene diamine was obtained from Aldrich Chemical Co. and hydrogenated, (700–900 psig H₂, 110°C, 5 hrs, in *t*-butanol) to give a 77/23 *cis/trans* isomer mixture of 1,4-cyclohexane diamine which was then phosgenated to give 1,4-cyclohexane diisocyanate. Various amounts of this material were mixed with 100% *trans* CHDI to obtain a homogeneous mixture of CHDI with various isomer distributions (Table I).
- 1,4-Butanediol (BDO) was obtained from Aldrich Chemical Co. in a Gold Label grade. This material was used as received.
- Voranol™ 5287 (V5287), manufactured by The Dow Chemical Company, is an ethylene oxide capped, poly(propylene glycol) of 2000 *M_n*. This material was used as received.
- H₁₂MDI was obtained from Mobay Chemical Co. (Desmodur™ W) This material was used as received.
- Isonate™ 125M (MDI), manufactured by The Dow Chemical Company, was purified by vacuum distillation prior to use (187°C at 3.3 mmHg).
- Dibutyltin dilaurate catalyst was obtained from M & T Chemicals (T-12). This material was used as received.

Table II Polymer Plaque Formulations

Sample	Index	Wt % Iso	Wt % BDO	Wt % V5287	Post Cure	Wt % H.S.
VII	1.028	24.77	10.45	64.78	16 hr	35
VIII	1.031	24.97	10.35	64.67	16 hr	35
IX	1.030	25.21	10.36	65.14	16 hr	35
X	1.030	28.19	6.71	65.10	16 hr	35
XI	1.029	28.33	6.72	64.95	16 hr	35
XII	1.028	25.03	9.71	64.68	16 hr	35

Table III Diisocyanate Used in Polymer Plaques

Sample ID	Diisocyanate Used
VII	100% <i>trans</i> CHDI
VIII	70% <i>trans</i> CHDI
IX	58% <i>trans</i> CHDI
X	MDI
XI	H ₁₂ MDI
XII	23% <i>trans</i> CHDI

- Dimethyl acetamide (DMAc) was obtained from Aldrich Chemical Co. in Gold Label grade in Sure Seal bottles. This material was used as received.

Characterization

Thermal Analysis

The following DuPont modules were interfaced with a model 2100 computer/controller and used to analyze samples; 983 DMA, 910 DSC, 951 TGA, 943 TMA. All work was performed under a nitrogen purge with heating rates of 3°C/min, 10°C/min, 10°C/min, and 5°C/min, respectively.

WAXS

A Siemens D-500 diffractometer equipped with a Co tube, primary beam monochromator, 1° slits and position sensitive detector was used to measure percent crystallinity. Power settings were 40 kV and 25 mA. Scans were obtained at a rate of 1°/min between 4° and 60° 2 θ .

Transmission Electron Microscopy (TEM)

The sample was stained with osmium tetroxide solution for 45 h. Microtoming was done at -95°C to produce 70 nm sections. Print magnification was 26,250 \times .

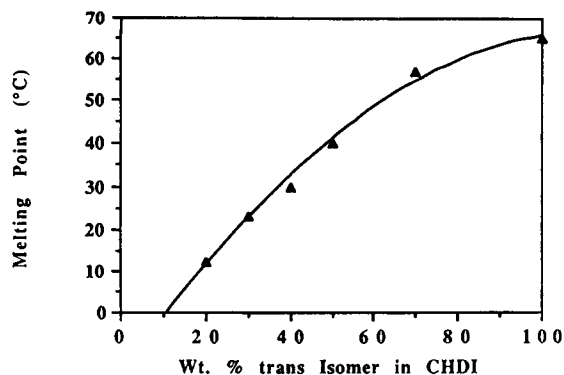


Figure 1 Melting point vs. wt % *trans* isomer in CHDI.

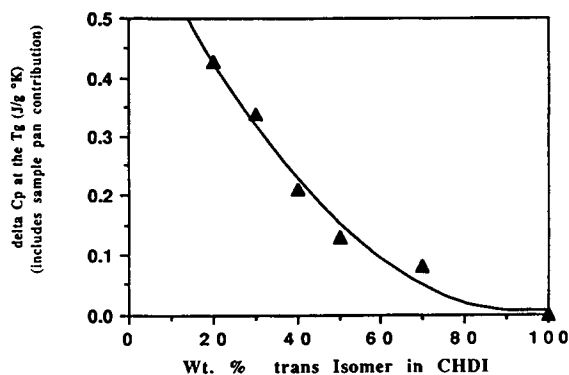


Figure 2 ΔC_p vs. wt % *trans* isomer in CHDI.

FT-IR

Work was done on a Nicolet 5-MX instrument at 4 cm^{-1} resolution with a nitrogen purge.

SYNTHESIS

Model Hard Segments

A three-necked, round-bottomed flask was dried for one hour at 150°C then equipped with a thermometer, rubber septum, gas inlet, and magnetic stirbar. The flask was purged with argon and then charged with 50 mL of dimethyl acetamide (DMAc). The flask was then heated to 60°C in an oil bath and the appropriate amounts of CHDI and BDO were added at a 1 : 1 stoichiometry, via a syringe through the septum, to make a 10% wt/wt solids solution. The solution was stirred at 60°C until an IR scan showed no free diisocyanate present (about 3 h) after which the product was precipitated by pouring the solution into 1.5 L of methanol. The precipitate was filtered and rinsed with methanol. The precipitate was dried in a vacuum oven overnight before being analyzed. The isomer distributions in the CHDI used to make the model hard segment polymers are shown in Table I.

Polymer Plaques

A two-step prepolymer process was used to make the polyurethane elastomer plaques. A 100 mL resin kettle was equipped with a thermometer, addition funnel, mechanical stirrer, and a gas inlet. The system was purged with argon and maintained under an argon cover. The kettle was heated to about 65°C in an oil bath and then charged with the appropriate amount and type of diisocyanate (Tables II and III). When the diisocyanate was completely melted, the

Voranol™ 5287 was added dropwise through the addition funnel over a 45-min period. The resulting isocyanate functional prepolymer was checked at various times to determine the equivalent weight and thus extent of reaction. This was determined using a standard HCl/di-*n*-butyl amine titration (ASTM D-1638-74).

When the prepolymer reaction was complete, 75 g of prepolymer were poured into a disposable plastic beaker and degassed in a vacuum desiccator for one minute. The appropriate amount of previously degassed BDO (Table II) and enough T-12 catalyst to give a 2-min gel time were added to the beaker and then mechanically stirred for 20 seconds. The contents of the beaker were then degassed for 30 seconds before being poured into a $4'' \times 4'' \times 0.125''$ steel window mold. The mold was then placed in a hydraulic press at 2000 psi and 130°C overnight. The mold was then allowed to cool and the plaque removed.

All plaques were formulated to give a hard segment concentration of 35 wt % with an index (ratio of isocyanate to hydroxyl groups) of 1.03. Thirty-

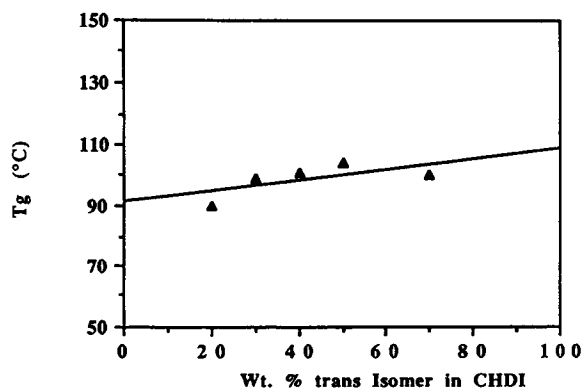


Figure 3 T_g vs. wt % *trans* isomer in CHDI.

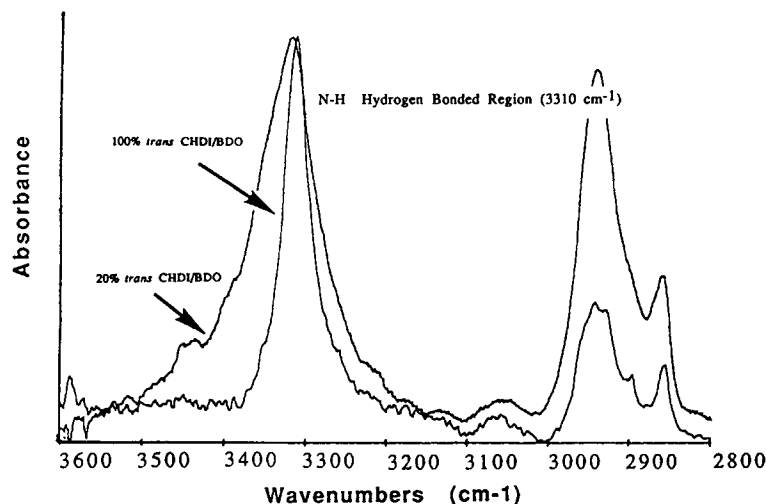


Figure 4 FT-IR of N—H bonded region.

five weight percent was the maximum amount of hard segment that could be formulated in the prepolymer without having the excess CHDI crystallize out and form a paste when the prepolymer cooled down to room temperature.

The CHDI plaques made at 35 wt % hard segment were an opaque white color while one made at 25 wt % hard segment was clear, as was the plaque made with H_{12} MDI. The plaque made with MDI was an opaque pale yellow color.

RESULTS AND DISCUSSION

CHDI Monomer Mixtures

Figure 1 shows a plot of melting point versus weight percent *trans* isomer in the CHDI mixtures used for this study. The increase in melting point with increasing *trans* isomer content is clearly visible. Since a liquid is the most desirable from a processing point of view, the ease of handling and processing will decrease with increasing *trans* isomer content in the CHDI. However, the 50% *trans* CHDI has a melting point of 40°C which is approximately equal to that of MDI, a widely used commercial diisocyanate.

Model Hard Segments

The model hard segments were made such that the only variable present was the variation in the CHDI isomer distribution. Differential Scanning Calorimetry (DSC) was used to investigate the morphology of these polymers. Each sample was heated to

250°C (1st scan) then quench cooled to -150°C and reheated to 250°C (2nd scan). The first scans showed a glass transition (T_g) at about 91°C and a melting endotherm (T_m) at about 161°C for the 20% *trans* polymer. This endotherm showed a decreasing ΔH_m and a slight increase in the melting temperature as the amount of *trans* isomer in the model hard segment was increased. The glass transition decreased in size with increasing *trans* isomer content and was not visible above a 40% *trans* concentration in the first DSC scans.

Second DSC scans showed a glass transition at about 98°C and a recrystallization exotherm (T_c) at about 155°C. The height of the T_g , as measured by DSC, can be related to the ΔC_p which in turn

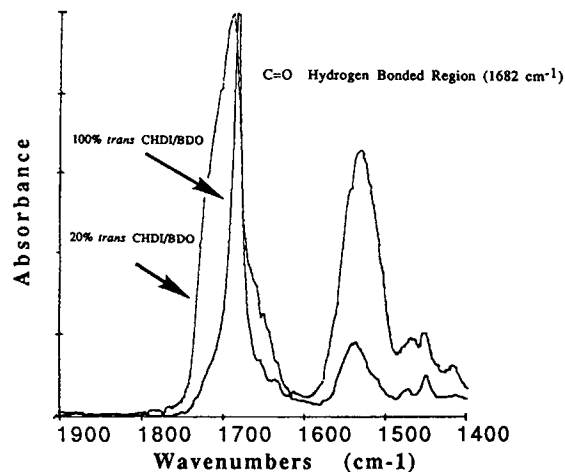


Figure 5 FT-IR of C=O Bonded Region.

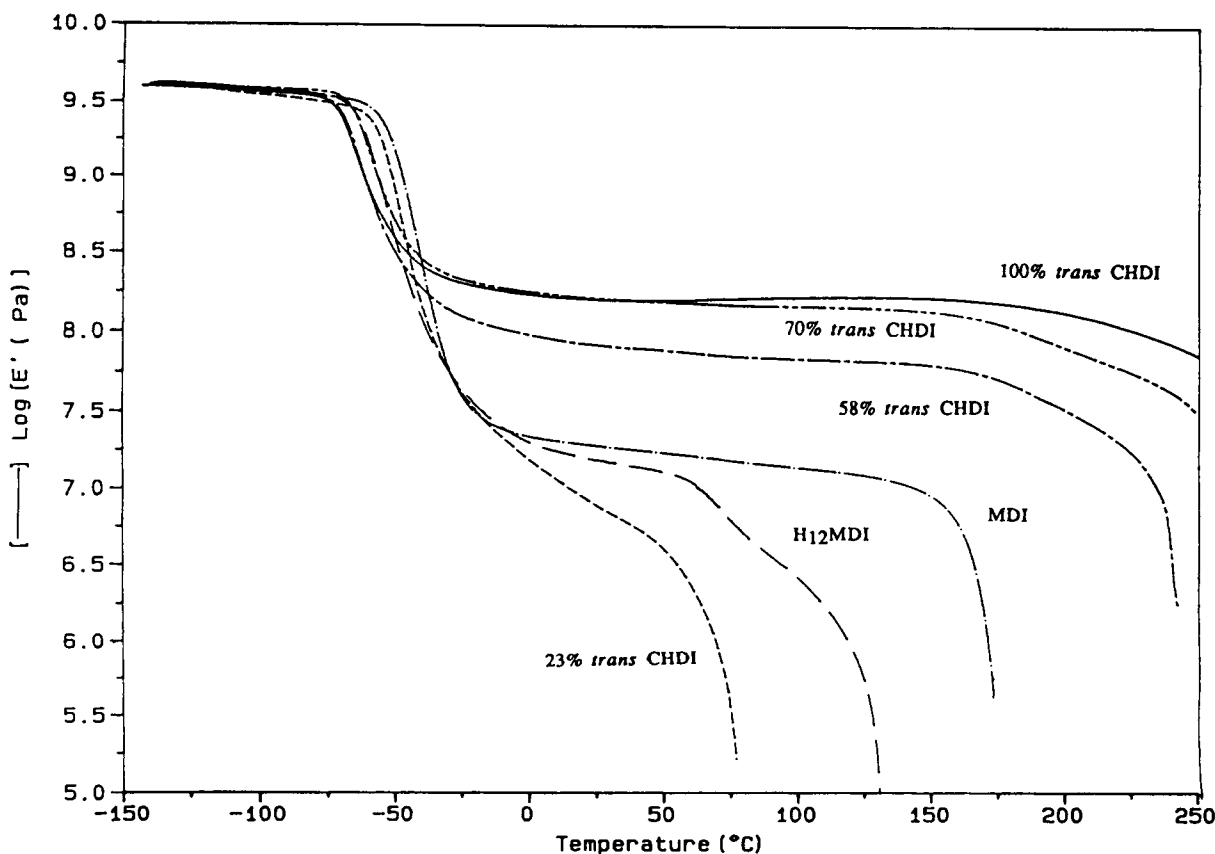


Figure 6 DMA of polymer plaques.

relates to the amount of amorphous material present in a sample. These T_g heights, reported as ΔC_p s, plus the contribution from the sample pans for the second scans, are plotted in Figure 2 and tabulated in Table VII. This figure shows that as the *trans* content is increased, the size of the T_g decreases, with the 100% *trans* model hard segment showing no transitions by DSC. Figure 3 shows that the glass transition temperature is relatively constant up to a 70% *trans* isomer distribution.

Figures 2 and 3 show that the fraction of material undergoing the glass transition is decreasing, indicated by the size of the T_g , but the morphology of

this material is not changing, indicated by the relatively constant position of the T_g . This gives a good indication that the model hard segment has a block copolymer morphology, made of *trans* CHDI/BDO and *cis* CHDI/BDO blocks, as opposed to a random copolymer morphology. The DSC data indicates that the *cis* isomer blocks are responsible for all the thermal transitions seen by DSC. The *trans* isomer blocks would appear to be either crystalline with a mp above their decomposition temperatures, amorphous with a T_g above their decomposition temperatures, or a mixture of both.

FT-IR scans are shown in Figures 4 and 5. There

Table IV E' (Kpsi) Data for Polymer Plaques

Sample ID	25°C	50°C	100°C	150°C	200°C	225°C
VII	22,581	22,590	23,040	22,150	17,066	13,650
VIII	21,212	17,750	17,197	15,210	8,656	6,094
IX	11,880	11,060	9,528	8,763	4,857	2,806
X	2,504	2,247	1,796	1,193	—	—
XI	1,763	1,413	1,193	—	—	—
XII	1,269	666	—	—	—	—

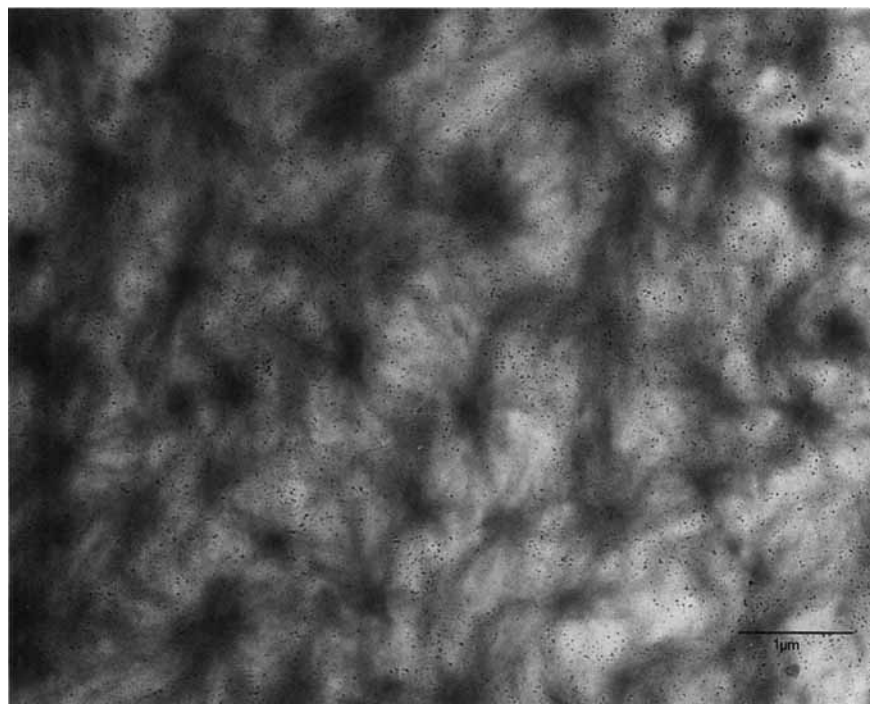


Figure 7 TEM of sample VII (100% *trans* CHDI).

is no scale on the absorbance axis since the scans have been autoscaled to fit on the page. The stronger looking intensity of the peaks in the C—H stretching region for the 20% *trans* CHDI model hard segment is also an artifact of autoscaling. The model hard segments made using 20% *trans* CHDI and 100% *trans* CHDI were examined. Figure 4 shows a peak for hydrogen bonded N—H at 3310 cm^{-1} . The polymer made from 100% *trans* CHDI/BDO shows a much narrower peak than the polymer made from 20% *trans* CHDI/BDO. This trend is also shown in Figure 5 which shows the hydrogen bonded carbonyl

region at 1682 cm^{-1} . The narrowness of the peaks are consistent with a narrower distribution of hydrogen bond lengths. This narrowness of hydrogen bond length distribution indicates a higher degree of ordering in the polymer as its *trans* CHDI content is increased.

Polymer Plaques

Flexural storage moduli (E') data for these elastomer plaques are plotted in Figure 6 and tabulated in Table IV. It can be readily seen that increasing the

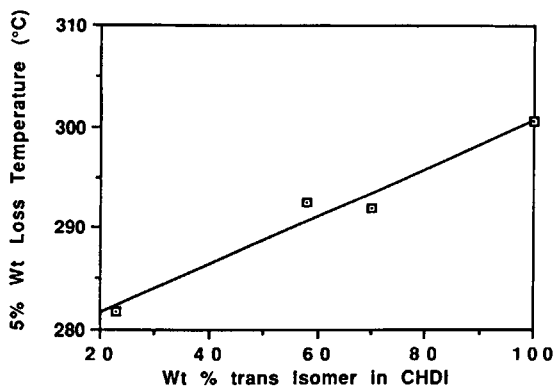


Figure 8 5% Wt. loss temperature vs. wt % *trans* isomer in CHDI.

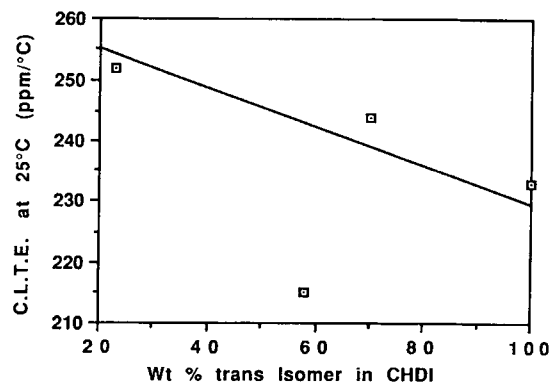


Figure 9 C.L.T.E. vs. wt % *trans* isomer in CHDI.

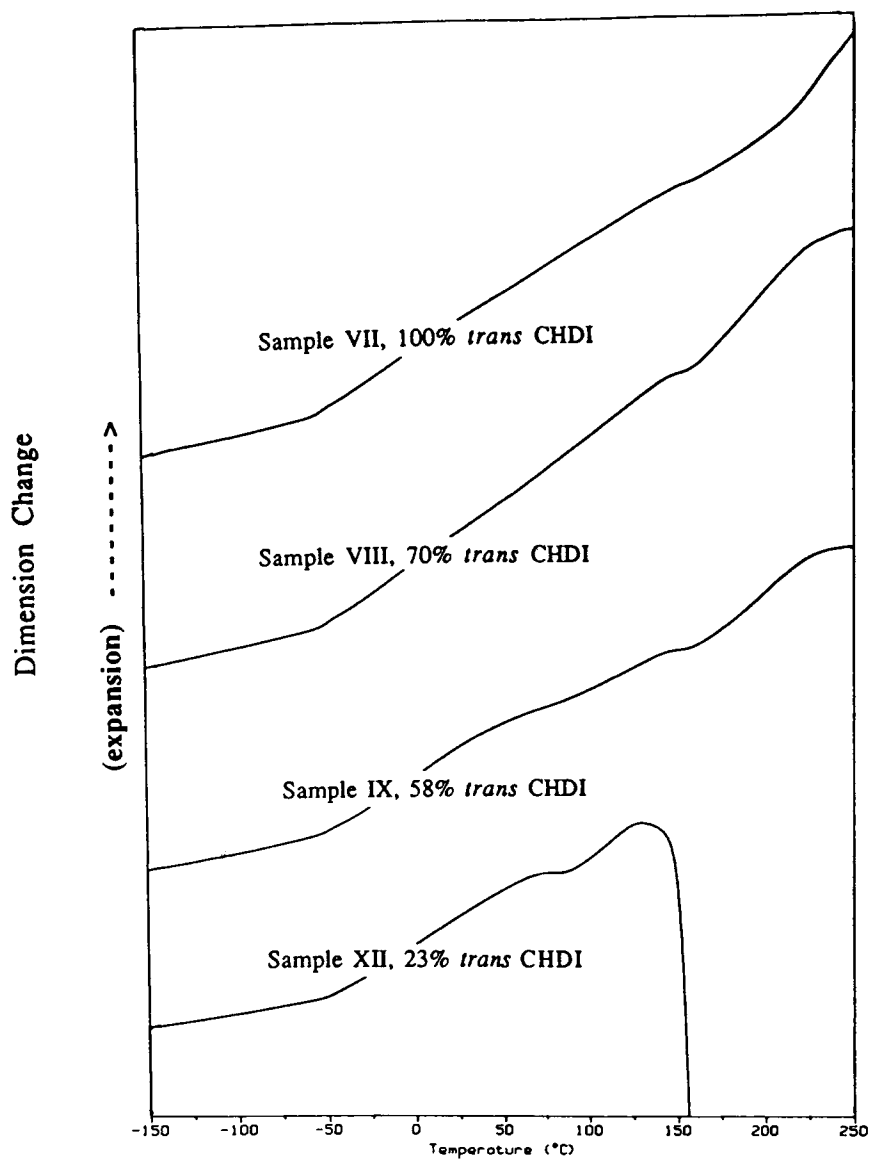


Figure 10 TMA scans for samples VII, VIII, IX, and XII.

trans content of the CHDI produces significant increases in E' throughout the rubbery plateau region. These polymers also show excellent phase separation between the hard segment and soft segment blocks

as indicated by the flat rubbery plateau region up until the point where the *cis* hard segment block transitions (T_g , T_m) start to occur. The plaque made with 100% *trans* CHDI shows a modulus increase

Table V WAXS Data (in Wt %)

Sample ID	Crystalline Phase	Amorphous Phase	Semicrystalline	Wt % <i>trans</i> CHDI
VII	11.3	75	14	100
VIII	7.0	78	15	70
IX	6.0	79	15	58
XII	2.4	87	11	23

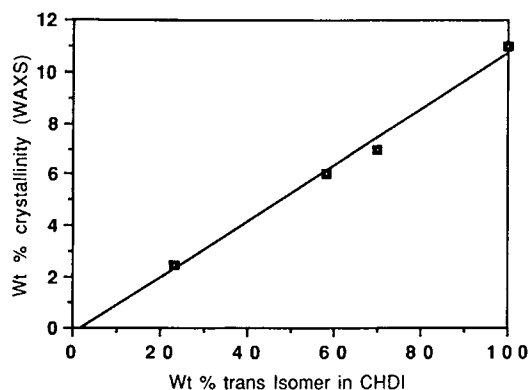


Figure 11 Wt % crystallinity vs. wt % *trans* isomer in CHDI.

between 50°C and 125°C. This increase is still present when the sample is cooled down and scanned a second time and is believed to be a thermoelastic inversion effect. When compared to the plaques made with MDI and H₁₂MDI, the CHDI plaques show up to a tenfold increase in modulus.

A TEM micrograph for plaque VII (100% *trans*), Figure 7, shows the soft segment as a white, continuous phase. The tiny dots visible throughout the micrograph are an artifact. The hard segment domains appear as dark spherulitic type structures with diameters in the micron range. Many of these domains have a size approaching the wavelength of visible light. This could help explain the opacity of the plaques at 35 wt % hard segment and the fact that a plaque made at 25 wt % hard segment, which would have even smaller hard segment domains, is transparent.

TGA data are shown in Figure 8. A trend of increasing thermal stability with increasing *trans* CHDI concentration is readily observed. The TMA

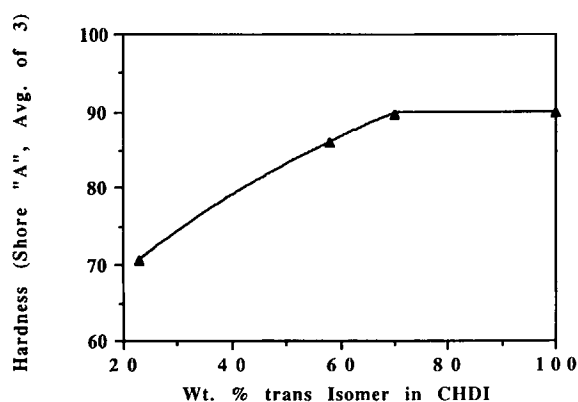


Figure 12 Hardness vs. wt % *trans* isomer in CHDI.

Table VI Hardness for Polymer Plaques (Av of 3)

Sample	Shore 'A'
VII	90.0
VIII	89.7
IX	86.0
X	76.0
XI	74.7
XII	70.7

data are shown in Figures 9 and 10. Figure 9 shows a trend of decreasing C.L.T.E. values with increasing *trans* CHDI content in the polymer, though the polymer made with 58% *trans* CHDI appears to be somewhat of an anomaly.

Since these polymers were made at a relatively low hard segment content, the more sensitive TMA was used, as opposed to DSC, to look at morphology. Figure 10 shows a composite of TMA scans for samples VII, VIII, IX, and XII. The transitions seen here correspond well with what was seen in the model hard segment study, though it should be kept in mind that the hard segment chains have a lower molecular weight in these these elastomer plaques and that the large amount of soft segment also tends to shift the transition temperatures somewhat. The T_g s and T_m s appear as softening points and negative dimension changes are due to the 1-g load used for the procedure.

WAXS data was used to determine the weight percent crystallinity of the polymer plaques. The scans showed each sample to have an amorphous region, a crystalline region and a semicrystalline region. The distributions of each are shown in Table V.

When the WAXS data is plotted as weight percent crystallinity versus isomer distribution of the

Table VII ΔC_p (Plus Sample Pan Contribution) Versus Wt % *trans* Isomer in CHDI Model Hard Segments

ΔC_p (J/g °K)	Wt % trans Isomer
0.43	20
0.34	30
0.21	40
0.13	50
0.08	70
0.00	100

CHDI used (Figure 11) it is readily observed that when the *trans* isomer content is increased the amount of crystallinity in the hard segment increases. However, we are only seeing 2% to 11% crystallinity out of a possible 35%. While it is possible for polymers with a low amount of crystallinity to show significant modulus increases with only a small increase in crystallinity, there may be an additional reason for the significant modulus increases we have seen.

The model hard segment data discussed previously showed the 100% *trans* CHDI/BDO model hard segment to have no thermal transitions, (T_g s, T_m s or T_c s), visible by DSC below 250°C. This means that when amorphous *trans* CHDI/BDO model hard segment, with a $T_g > 250^\circ\text{C}$, is mixed with *cis* CHDI/BDO model hard segment, which has a T_g of 98°C, a stiffer polymer with increased E' will result. The semicrystalline region, whose concentration does not change with varying isomer distribution, would then seem to be composed of amorphous and crystalline *trans* CHDI/BDO blocks.

Hardness data is shown in Figure 12 and Table VI. The hardness is seen to increase with increasing *trans* CHDI content as expected due to the higher crystallinity and ordering of this isomer.

SUMMARY AND CONCLUSIONS

Polyurethane elastomers based on 100% *trans* CHDI have been shown to give high performance properties.¹⁻⁵ This study examined the effect on polymer properties of using CHDI with various isomer distributions. The first part of the study examined the thermal properties of model hard segments made from CHDI and BDO. DSC analysis of these model hard segments showed them to have a block copolymer morphology composed of *trans* CHDI/BDO and *cis* CHDI/BDO blocks. The *cis* CHDI/BDO blocks showed a T_g of 98°C and a melting point of 161°C.

The 100% *trans* CHDI/BDO model hard segment showed no thermal transitions below 250°C.

The second part of our study involved making polyurethane elastomers from a polyether polyol, BDO, and CHDI with various isomer distributions. These polymer plaques, made such that the only variable involved was the CHDI isomer distribution, showed significant property differences. WAXS data showed that the polymers became more crystalline with increasing *trans* CHDI content and that a semicrystalline phase was present along with an amorphous phase. The increasing crystallinity is not surprising considering the small, compact, symmetrical structure of *trans* CHDI. The amorphous *trans* CHDI, which shows no T_g below 250°C, acts much like crystalline *trans* CHDI in terms of improving a polymer's properties.

The property improvements brought about by increasing the *trans* CHDI content, manifested themselves in lower C.L.T.E., higher thermal stability, greater hardness, and higher flexural storage modulus values. Comparisons with plaques made using MDI or H₁₂MDI showed these diisocyanates to give poorer properties when compared to plaques made using CHDI with an isomer distribution above about 50% *trans*.

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