

# Sensitivity to the Physical and Chemical Structure of Hard-Segment-Reinforced Polyurethane Elastomers with Variable Percentage of Hydrogen Bonding

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**ABSTRACT:** A series of segmented polyurethane elastomers was achieved with similar structures but with various percentages of hydrogen bonding. The effect of the hard segment (crystallizing or not) was followed by the inclusion of a conventional rigid diisocyanate, 4,4'-diphenyl methane diisocyanate, and an isocyanate with a large conformational mobility, 4,4'-dibenzyl diisocyanate. Hydrogen substitution was carried out with the following procedures: (1) the substitution of hydrogen bonding by direct exchange with deuterium of liquid D<sub>2</sub>O, (2) deuteration by synthesis with deuterated chain extenders (CEs) or deuterated macrodiols (MDs), and (3) hydrogen substitution with inert -CH<sub>3</sub> groups. The stress-strain data and

hysteresis in uniaxial tension indicated a dramatic softening and weakening when the hydrogen of the urethane groups was replaced by inert -CH<sub>3</sub> groups, which were incapable of undergoing intermolecular interactions. This was in contrast with the observations made on the materials synthesized with deuterated CEs, where the elastomeric behavior of the materials was observed to improve. For the materials obtained with deuterated MDs, significant modifications in the mechanical response were not observed relative to the analogous normal materials. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3544–3550, 2011

**Key words:** crystallization; crosslinking; hydrogen-bonding

## INTRODUCTION

Polyurethanes (PUs) are extensively hydrogen-bonded. Hydrogen bonding in PUs can be readily detected and studied by IR spectroscopy. The hydrogen-bonded and free N-H and urethane carbonyl C=O are peaks of interest.<sup>1–5</sup> The effect of hydrogen bonding is frequently used to explain various anomalies or improved properties. However, it is difficult to isolate this effect from the effects of the physical and chemical structure. Some studies have concluded that molecular mobility is not controlled by hydrogen bonding.

The hydrogen-bonding interaction in PUs is illustrated in Figures 1–3.

It is believed that a rapid increase in the molecular mobility accompanying the glass transition allows hydrogen bonds to dissociate.<sup>1–3</sup> Therefore, hydrogen bonding does not necessarily enhance the mechanical properties, although there is insufficient published data that quantitatively demonstrates the effect of hydrogen bonding on the mechanical properties.

To unambiguously distinguish the effects of hydrogen bonding requires that mechanical tests be

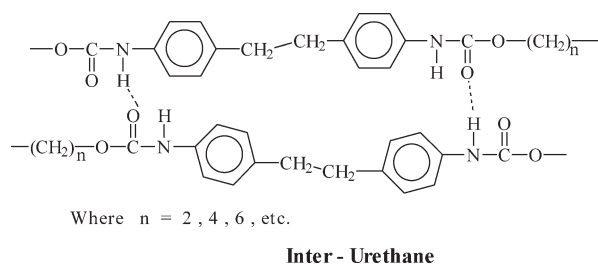
carried out on PUs of similar structures with and without hydrogen bonding.

Therefore, in this work, this problem was addressed by the study of a series of PUs with similar structures, achieved with or without hydrogen bonding or by gradual reduction of the hydrogen percentage. Hydrogen replacement was made by the substitution of hydrogen with deuterium or with inert -CH<sub>3</sub> groups.

The effect of hard segments (crystallizing or not) was also followed by the inclusion of two diisocyanates (DIs): a conventional rigid DI, 4,4'-diphenyl methane diisocyanate (MDI), or a DI with a large conformational mobility, 4,4'-dibenzyl diisocyanate (DBDI). The conformational mobility of DBDI caused an unusually wide range of physical and chemical properties, associated with the possibility of pronounced phase separation into a domain-matrix morphology, and with a higher tendency of crystallization and self-association by hydrogen bonding.<sup>6–10</sup>

The effect of hydrogen substitution with inert -CH<sub>3</sub> groups on the PUs mechanical response was also followed. The partial hydrogen substitution with inert -CH<sub>3</sub> groups (8, 23, and 80%) or the complete 100% replacement of hydrogen was carried out with the following synthesis routes: (1) by chemical modification of the usual PUs by substitution after synthesis with lithium hydride and methyl chloride and (2) by the use of dichloroformyl based on

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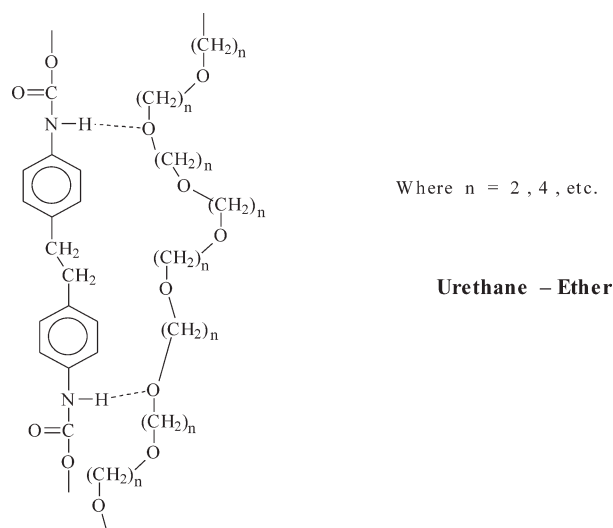
**Figure 1** Interurethane hydrogen-bonding interaction in PUs.

poly(ethylene adipate glycol) (PEA) or polytetrahydrofuran (PTHF) and the chain extenders (CEs) diethylene glycol (DEG) or butylene glycol (BG) reacted with  $N,N'$ -dimethyl diaminodiphenyl methane.<sup>11,12</sup>

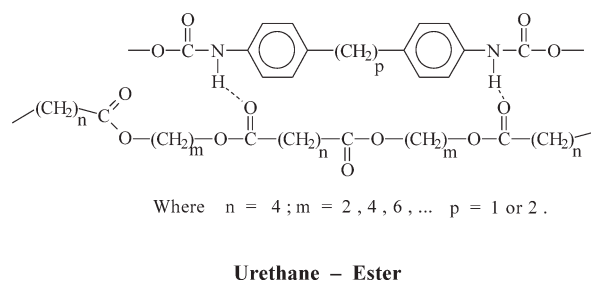
## EXPERIMENTAL

### Materials and polyaddition procedure

The family of PUs was synthesized for this work in the authors' Romanian laboratory. As outlined, they were all three-component systems combined in stoichiometric proportions and consisting of (1) a DI, either MDI or DBDI; (2) a macrodiol (MD), PEA or PTHF; and (3) a small-molecule diol as CE, anhydrous DEG, or BG. The MDs were all of molar mass  $2000 \pm 50$  g/mol. The three components were always mixed in molar proportions of HS:MD:CE of 4 : 1 : 3; this gave hard-segment (HS) mass fractions in the region of 40% and an isocyanic index ( $I$ ) of 100. Synthesis was carried out by the prepolymer route described previously by Prisacariu and coworkers.<sup>6,7,9</sup> The DI and MD components were reacted together with vigorous mixing *in vacuo* at 100°C to give a prepolymer consisting of MD terminated at each end by



**Figure 2** Urethane-ether hydrogen-bonding interaction in PUs.



**Figure 3** Urethane-ester hydrogen-bonding interaction in PUs.

DI. This was then thoroughly mixed with CE at 90°C. The cast melt was poured between Teflon plates for curing at 110°C over 24 h. The final result was polymer with a molar mass in the range 60–120 kg/mol in the form of 20- $\mu\text{m}$  thin films or sheets with thicknesses in the range 0.6–2 mm.

To replace hydrogen with deuterium, the films were suspended in 250-mL glass ampules that contained 5 mL of  $\text{D}_2\text{O}$  on the bottom. To achieve the PU sample dehydration, the inferior part of the glass ampule was cooled for 24 h with solid  $\text{CO}_2$ , vacuumed to 0.1 mmHg, and sealed *in vacuo*. For deuteration, the ampules were kept at room temperature and alternatively at 60°C for 24 h. The PUs films were then dried in closed precincts containing  $\text{P}_2\text{O}_5$ . The pressure of water vapors varied between values of 0.0004 mmHg (−80°C) and 149.3 mmHg (60°C; the corresponding values for  $\text{D}_2\text{O}$  were about equivalent).

For thicker ( $\leq 2$  mm) PU sheets, a similar procedure was carried out. To speed up the isotope exchange, we carried out a cyclic hydrating–dehydrating procedure in closed systems where the PU specimens were fixed in the upper part of the system. Heating–cooling cycles were repeated 17 times over 34 days, after which the degree of deuteration was followed by IR spectra.

The polyaddition procedures to obtain PUs where hydrogen was replaced with inert  $-\text{CH}_3$  groups were previously described elsewhere.<sup>11–13</sup> The materials based on deuterated PTHF were also obtained in the Romanian laboratory. The soft segments were obtained similarly as the analogous normal PUs with the DIs DBDI or MDI, and the CEs DEG or BG. The deuterated PTHF soft segment  $-\text{HO}-(\text{CD}_2)_4-\text{O}-\text{H}$  was obtained by the polymerization of 100% deuterated tetrahydrofuran with chlorosulfonic acid as a catalyst, according to the method described in Houben–Weyl (Makromolekulare Stoffe Teil 2).<sup>13</sup>

The normal materials (100% hydrogen) studied in this work were labeled Pu1–Pu8 according to their combinations of HS, MD, and CE, as indicated in Table I. It should be noted that the stoichiometric proportions used in these polymers ( $I = 100$ ) meant that they were truly thermoplastic. They did not have

**TABLE I**  
**Compositions of the Family of Normal PU Elastomers**  
**(with 100% Hydrogen Bonding): Pu1–Pu8 Prepared and**  
**Studied in This Work**

		PEA	PTHF
MDI	DEG	Pu1	Pu5
MDI	BG	Pu2	Pu6
DBDI	DEG	Pu3	Pu7
DBDI	BG	Pu4	Pu8

the potential for further reaction with ambient humidity to produce chain lengthening and allophanate crosslinking, as seen in similar polymers but with excess isocyanate groups (e.g.,  $I = 110$ ).<sup>5,9</sup>

The MDs used to obtain the materials were the polyesteric PEA and the polyetheric MD, PTHF. The CEs were two low-molecular-weight diols, DEG and BG.

Three subsets of deuterated PUs were obtained with the following preparation procedures: (1) the hydrogen exchange with deuterium of liquid  $D_2O$  after material synthesis, (2) the deuteration by synthesis with deuterated CEs, and (3) the deuteration by synthesis with deuterated soft segments (PTHF) of molar mass  $2000 \pm 50$  (Fig. 4).

### Mechanical tests

The polymers in the form of films prepared as described previously were subjected to uniaxial tensile tests at a constant nominal strain rate. In addition, to investigate mechanical hysteresis, cyclic tensile tests were carried out; we cycled between a fixed strain limit and zero load, using a constant nominal strain rate of magnitude  $0.03 \text{ s}^{-1}$ . No dwell time was allowed when the straining changed direc-

tion. Test specimens were cut from films of dimensions given in ASTM D 1708, that is, dumbbell-shaped specimens with a length of 53 mm between shoulders, a gauge length of 20 mm (on which the strain was measured), a width of 5.8 mm, and thicknesses of 0.3–2 mm. The stress–strain data on these specimens presented here were obtained with an Instron 4204 testing machine or a Schopper MZ grip testing machine at room temperature ( $T \approx 25^\circ\text{C}$ ). Strain was measured manually from the movement of fiducial marks or from grip displacement after we used video images of the gauge length to correct for nonuniform strain outside the gauge length.

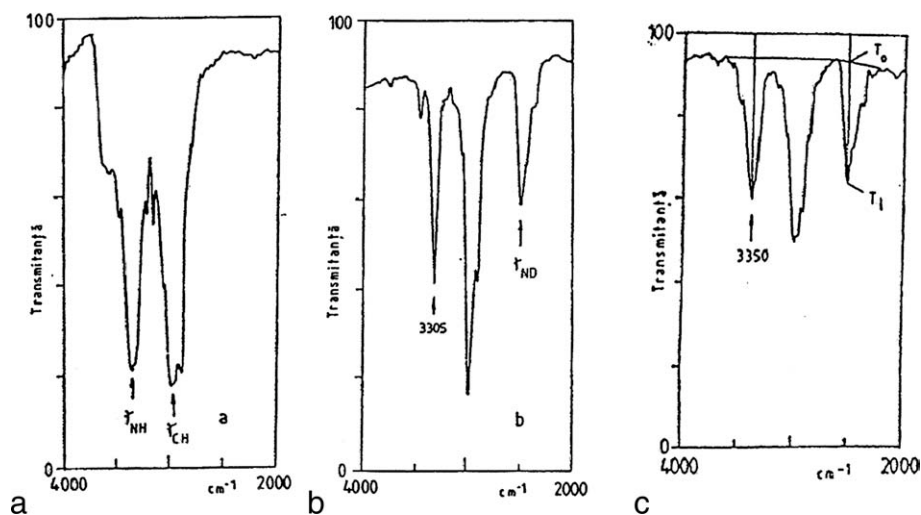
## RESULTS AND DISCUSSION

### Deuterated materials obtained by direct exchange of hydrogen with deuterium of liquid $D_2O$ after PU synthesis

A subset of deuterated materials was obtained as described earlier, where hydrogen was substituted with deuterium of liquid  $D_2O$  after material synthesis. This gave a significant exchange of about 65% not at room temperature but at  $60^\circ\text{C}$  and only for the materials in the form of 20- $\mu\text{m}$  thin films. In the case of thicker (up to 2 mm) PUs sheets, the direct exchange of hydrogen with deuterium with vapors of  $D_2O$  failed because of the higher volume of the  $D_2O$  molecules unable to penetrate through thicker PUs macromolecular networks.<sup>12</sup>

### Deuterated materials obtained with deuterated CEs or deuterated MDs

To enable the replacement of hydrogen with deuterium in the case of thicker materials, we employed



**Figure 4** Sample IR spectra of Pu3 (DBDI:DEG:PEA): (a) normal PU with hydrogen bonding, (b) deuterated material obtained by the direct exchange of hydrogen with deuterium of  $D_2O$ , and (c) deuterated PU obtained with a deuterated CE and DEG.  $T_0$  = transmitted intensity at the baseline;  $T_1$  = IR radiation transmitted to the sample;  $\nu_{\text{NH}}$  = absorption frequency for NH group,  $\nu_{\text{CH}}$  = absorption frequency for CH group,  $\nu_{\text{ND}}$  = absorption frequency for ND group.

deuteration by synthesis by using a deuterated MD (PTHF) or a deuterated CE,  $\text{DO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{OD}$  (DEG d; isotopic purity = 90%) instead of a normal DEG. DEG d was obtained from a mixture of  $\text{D}_2\text{O}$  and DEG (25 : 6 vol %) by fractionated distillation after 24 h of isotopic exchange at  $60^\circ\text{C}$ . Quantitative measurements confirmed a 66.7% deuteration degree.<sup>12</sup> PUs with deuterated soft-segment PTHF were obtained as described earlier.

### IR spectra

We carried out IR measurements to estimate the degree of isotope exchange by following the decrease of the  $\nu_{\text{NH}}$  stretching vibration and, concomitantly, the increase of  $\nu_{\text{ND}}$  corresponding to the step-by-step appearance of the ND groups as a result of hydrogen replacement with deuterium (Fig. 4).

As seen in Figure 4, the position of the urethane hydrogen replacement was strongly influenced by the choice of polyaddition procedure adopted. After deuteration with  $\text{D}_2\text{O}$  vapors, instead of the prominent  $3300\text{--}3400\text{ cm}^{-1}$  N—H stretching band [Fig. 4(a)], there remained only a band centered at  $3305\text{ cm}^{-1}$  [Fig. 4(b)], which corresponded to the most associated state. In the case of the materials synthesized with a deuterated CE [Fig. 4(c)], compared to the large  $3300\text{--}3400\text{-cm}^{-1}$  N—H stretching band, there was only a narrow band centered at  $3350\text{ cm}^{-1}$ , which corresponded to the lowest associated state.

We deduce, therefore, that in the case of deuterated glycols, hydrogen replacement occurred preferentially at the junction points between the hard segments and polyesters, whereas in the case of deuteration by the direct exchange of hydrogen, the replacement of hydrogen proceeded mainly within the middle of the hard-segment urethane groups.

The degree of deuteration was calculated on the basis of the ratio between the absorption intensities of the NH and ND groups as follows:

$$\text{Deuteration}(\%) = \frac{A_{\text{NH}} \times 1.428}{A_{\text{ND}} \times 1.428 + A_{\text{NH}}} \quad (1)$$

where  $A_{\text{ND}}$  and  $A_{\text{NH}}$  are the IR absorbances of the NH and ND stretching vibrations, respectively.<sup>13</sup> The percentage of hydrogen bonding was investigated by means of NMR studies. PU-cast melt sheets were turned into films obtained by their dissolution in dimethylformamide, followed by evaporation from solution.

### PUs mechanical response

In PU elastomers, the resilience of the material is an important attribute. The choice of material for any given application then hinges on a spectrum of key

properties offered by relatively soft polymers, stiffness and strain recovery characterizing their elasticity but also inelastic effects such as hysteresis and stress relaxation. As shown elsewhere, in these respects, the mechanical properties of the normal PUs (Table I) with hydrogen studied in this work were similar to those of other thermoplastic elastomers, but their performance as elastomers was shown to vary greatly, depending on the chemical composition. As previously shown elsewhere, first, loading to a given deformation was associated with higher stiffness and hysteresis than is typical for a homogeneous crosslinked elastomer, especially in the case of DBDI-based materials. First-cycle hysteresis was found to increase with reduced phase separation and with replacement of MDI by DBDI.

As we<sup>5-10</sup> and Lyman et al.<sup>14</sup> reported earlier, the MDI molecule introduced the rigid  $-\text{Ph}-\text{CH}_2-\text{Ph}-$  moiety into the elastomeric PU hard segments. In contrast, when we used DBDI, the specific  $-\text{Ph}-\text{CH}_2-\text{CH}_2-\text{Ph}-$  moiety introduced a variable geometry into the hard segments because of the possibility of internal rotation of this isocyanate around the  $-\text{CH}_2-\text{CH}_2-$  ethylene bridge. This led to the appearance of both syn and anti rotational conformations, which coexisted in the DBDI-based PU macromolecules. As a result, in this latter case, the PU macromolecules could adopt more compact packing, which significantly enhanced the ability to order in crystalline structures predominantly involving the anti form.<sup>6,7</sup>

In this study, the subset of normal materials listed in Table I and their analogous structures achieved with deuterated CE or MD were subject to a series of cyclic uniaxial tensile tests at room temperature and ambient humidity; this study was designed to characterize features of their mechanical response relevant to their performance as thermoplastic elastomers, with a special focus on their stiffness, (Tables II–IV). PUs performance as elastomers was assessed by means of a series of cyclic tensile tests, cycling between 300% elongation and zero load with a constant nominal strain rate of magnitude,  $0.03\text{ s}^{-1}$ . No dwell time was allowed when the straining changed direction.

PUs cyclic responses were studied with respect to their chemical composition as follows: materials based on normal or deuterated CE (DEG; Table II) and materials derived from normal or deuterated MD (PTHF; Tables III and IV).

From these tests, the initial input strain energy density ( $E_{1C}$ ) was computed as the area under the first-cycle loading curve of nominal stress versus nominal strain up to the elongation limit of 300%. The calculation was repeated for the corresponding quantity for the second load cycle [strain energy density of the second load cycle ( $E_{2C}$ )]. Similarly, the

TABLE II

Example Tensile Properties of a Polyetheric DBDI-Based PU Obtained with Normal (PTHF) and Normal or Deuterated DEG

Tensile property	Normal DEG	Deuterated DEG
100% tensile stress (MPa)	5.2	7.3
300% tensile stress (MPa)	8.8	10.4
Tensile strength (MPa)	50.6	69.2
Residual elongation (%)	48.0	22.0
Shore A hardness	90	94
$E_{1C}$ (MJ/m <sup>3</sup> )	26.3	26.1
$E_{1R}^*$ (%)	16.2	16.1
$E_{2C}^*$ (%)	50.8	50.2
$E_{2R}^*$ (%)	16.6	16.0
$E_{1H}^*$ (%)	50.2	49.4
$E_{2H}^*$ (%)	46.8	46.3

The normal material is Pu7 in Table I.  $E_{1H}$  and  $E_{2H}$ , fractional hysteresis energy density of the first and second cycles, respectively.

recovered energy densities of the first and second cycles ( $E_{1R}$  and  $E_{2R}$ , respectively) were computed as the areas under the unloading curves for first and second cycles, respectively. The areas were measured on paper copies of the curves with a digital planimeter. In this article,  $E_{2C}$ ,  $E_{1R}$ , and  $E_{2R}$  are expressed as fractions of the  $E_{1C}$  and are denoted as such by an asterisk. The fractional energy dissipated on each cycle was expressed as the fractional hysteresis energy density on the first and second cycles, as previously described.<sup>7</sup>

As seen in Table II for example material Pu7, from the stress-strain data for uniaxial tension, it was observed that materials derived from deuterated CE were more resilient. This was due to the increase of the energy of association when we changed from hydrogen bonding to deuterium bonding, as observed by others in the case of low-molecular products.<sup>15</sup>

TABLE III

Example Tensile Properties for a DBDI-Based PU Obtained with Normal BG and Normal or Deuterated PTHF

Tensile property	Normal PTHF <sub>2000</sub>	Deuterated PTHF <sub>2000</sub>
100% tensile stress (MPa)	7.68	7.5
300% tensile stress (MPa)	11.3	10.8
Tensile strength (MPa)	57.4	56.1
Residual elongation (%)	280	270
Shore A hardness	90	91
$E_{1C}$ (MJ/m <sup>3</sup> )	40.8	40.1
$E_{1R}^*$ (%)	10.2	10.0
$E_{2C}^*$ (%)	35.7	34.8
$E_{2R}^*$ (%)	10.5	10.7
$E_{1H}^*$ (%)	86.7	85.9
$E_{2H}^*$ (%)	72.6	73.0

The normal material is Pu7 in Table I.  $E_{1H}$  and  $E_{2H}$ , fractional hysteresis energy density of the first and second cycles, respectively.

TABLE IV

Example Tensile Properties for an MDI-Based PU Obtained with Normal BG and Normal or Deuterated PTHF

Tensile property	Normal PTHF <sub>2000</sub>	Deuterated PTHF <sub>2000</sub>
100% tensile stress (MPa)	4.22	4.3
300% tensile stress (MPa)	8.9	9.4
Tensile strength (MPa)	38.9	37.6
Residual elongation (%)	40	20
Hardness, Shore A	90	94
$E_{1C}$ (MJ/m <sup>3</sup> )	29.9	29.5
$E_{1R}^*$ (%)	39.0	38.6
$E_{2C}^*$ (%)	64.0	63.5
$E_{2R}^*$ (%)	38.8	38.4
$E_{1H}^*$ (%)	54.7	54.1
$E_{2H}^*$ (%)	26.4	25.9

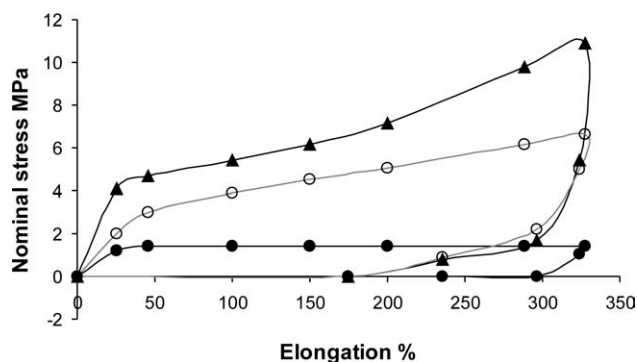
The normal material is Pu6 in Table I.  $E_{1H}$  and  $E_{2H}$ , fractional hysteresis energy density of the first and second cycles, respectively.

Comparing successive load-unload cycles (Figs. 5–7), we found that irreversible changes to the stress-strain response were confined essentially to the first loading cycle. In subsequent cycles, the load-unload stress-strain curves remained almost unchanged for all of the materials (normal and based on deuterated CE or deuterated soft-segment MD). For example, it may be seen from Table II–IV that  $E_{1R}$  and  $E_{2R}$  were equal in most cases to a good approximation. Similarly, increasing the time interval between the end of one unloading cycle and the start of the next from a few seconds to several hours (up to 24 h) had no sensible effect on the measured recoverable strain energy. This was in contrast to the input energy, which was clearly dependent on both the previous strain history and the relaxation time between loading cycles.<sup>7</sup>

The performance of these materials as elastomers was shown to vary greatly depending on the composition. Hysteresis and residual strain in the case of normal and deuterated BG–DBDI-based PUs were significantly greater than in the case of both the other two materials (noncrystalline and those based on either MDI or DBDI–DEG). The most extreme difference between the effects of the MDI and DBDI hard segments was seen in the cases of the CE–DI couple BG–DBDI, where the hard segments were observed to crystallize.<sup>6,7,9</sup> In such materials, the stiffness, hysteresis, and residual elongation were all increased relative to the corresponding MDI-based PU. When the couple was DEG–DBDI, the differences were less pronounced because DEG inhibited



Figure 5 Hydrogen substitution with inert  $-\text{CH}_3$  groups.<sup>13</sup>



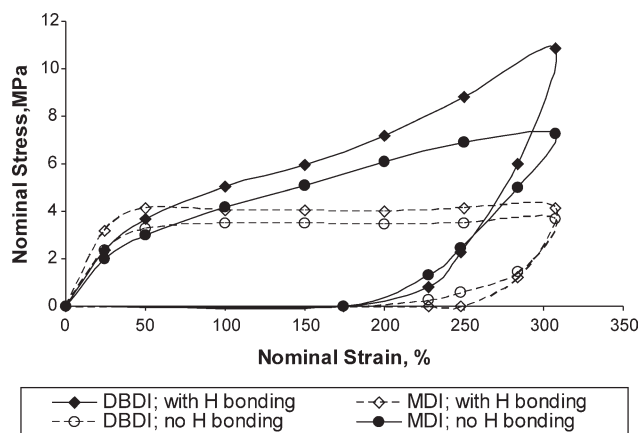
**Figure 6** First tensile load-unload cycles for material Pu8 (DBDI-BG-PTHF) at a strain rate of  $0.03 \text{ s}^{-1}$ , where hydrogen was substituted gradually with inert  $-\text{CH}_3$  groups. The %H/% $\text{CH}_3$  group ratios were ( $\blacktriangle$ ) 100/0, ( $\circ$ ) 80/20, and ( $\bullet$ ) 8/92.

crystallization of the hard segments. These differences between DBDI and MDI could be attributed to the greater flexibility of DBDI, which allowed a higher tendency toward self-association by hydrogen bonding.<sup>7</sup>

Changing the nature of the soft-segment MD (replacing normal PTHF with deuterated PTHF; Tables III and IV) had no sensible effect on the mechanical response of the materials for either hard segment, MDI or DBDI. However, regardless of the nature of the soft segment (normal or deuterated), the materials based on the couple BG-DBDI showed a higher  $E_{1C}$  and a lower fractional  $E_{1R}^*$  than the corresponding MDI and DBDI-DEG based PUs. We could also see consequences of differing chemical structures, which were replicated across the whole set of materials (MDI-based and DBDI-based), but those extended with DEG had a discernibly lower initial stiffness than the material based on DBDI-BG (Pu8), as revealed by the values of  $E_{1C}$  in Tables III-IV for example materials Pu7 and Pu6.

### Hydrogen substitution with inert $-\text{CH}_3$ groups

In the second stage of the study, a subset of PUs was achieved where the hydrogen of the urethane



**Figure 7** Examples of the first tensile load-unload cycles for materials Pu2 (BG-PEA-MDI) and Pu4 (BG-PEA-DBDI) at a strain rate of  $0.03 \text{ s}^{-1}$ , where hydrogen was totally substituted with inert  $-\text{CH}_3$  groups.<sup>13</sup>

group was replaced partially with  $-\text{CH}_3$  groups by a gradual decrease of the hydrogen percentage from 80 to 8%. To obtain these materials, the MDs PTHF and PEA of molar mass  $2000 \pm 50$  and BG were used. The materials were compared with similar structures where hydrogen was replaced 100% with inert  $-\text{CH}_3$  groups (Fig. 5).

Gradually decreasing the percentage of hydrogen resulted in decreases of the stresses in stress-strain data and the molecular weight values expressed as the inherent viscosity. This is shown in Table V for example PEA-based materials from Table I.

As seen in Table V and Figure 6, the PU's inherent viscosity and stress-strain response differed, depending on material's structure and percentage of decrease of hydrogen available for hydrogen bonding. The common feature for the materials listed in Table V was that the inherent viscosity and stress-strain data values decreased dramatically and proportionally with diminishing percentage of hydrogen (from 80 to 23 to 8%).

To assess what the main process was that caused the decrease of the stresses, we proceeded to the total replacement of hydrogen with inert  $\text{CH}_3$  groups.

**TABLE V**  
Inherent Viscosity and Nominal Stress at 300% Strain as a Function of the Percentage of Hydrogen for Selected PEA-Based Materials Listed in Table I

PU structure	Inherent viscosity (dL/g)		Nominal stress at 300% strain (MPa)		Tensile strength (MPa)		Percentage of H available for hydrogen bonding
	Initial 100% H	Modified	Initial 100% H	Modified	Initial 100% H	Modified	
DBDI-DEG-PEA (Pu3)	0.78	0.38	8.0	2.8	61.7	9.2	23
MDI-BG-PEA (Pu4)	1.16	0.24	11.5	—	61.5	3.4	8
DBDI-BG-PEA (Pu2)	0.62	0.52	15.7	8.4	50.8	36.1	80

**TABLE VI**  
**Example Stress–Strain Data of Material Pu4 (PEA–BG–DBDI): With and without Hydrogen**  
**(ratio of %H/%CH<sub>3</sub> groups: 100/0 % and 0/100 % respectively)**

PU synthesis route	Inherent viscosity (dL/g)	Shore A hardness	Stress at 300% strain (MPa)
With hydrogen bonding	1.24	90	12.8
Without hydrogen bonding	0.38	71	3.9
PU synthesis route	Tensile strength (MPa)	Elongation at break (%)	Residual elongation (%)
With hydrogen bonding	62.3	680	60
Without hydrogen bonding	6.7	770	220

As seen in Table VI and Figure 7, the 100% replacement of hydrogen with  $-\text{CH}_3$  groups resulted in a dramatic increase the materials' inelasticity, as revealed by a constant degree of elongation at break and by a dramatic increase of the residual elongation, which resulted in a pronounced tendency toward polymer plasticization. Inelasticity (residual strain, hysteresis) increased when hydrogen was substituted with inert  $-\text{CH}_3$  groups. Inelastic effects were even more pronounced when the hard segment crystallized, that is, when DBDI was used in the material synthesis.

As seen in Figure 7, hysteresis and residual strain were greater in the case of the material obtained with the CE–DI couple BG–DBDI, where the hard segments crystallized.

## CONCLUSIONS

A family of segmented PU elastomers was achieved with similar structures but with various percentages of hydrogen bonding. The performance of these materials as elastomers was followed. The effect of hard segments (crystallizing or not) was also investigated by the inclusion of two DIs: a conventional rigid DI, MDI, and a DI with a large conformational mobility, DBDI. When hydrogen was substituted by direct exchange with deuterium of liquid D<sub>2</sub>O after material synthesis, a significant exchange of about 65% was obtained for the materials in the form of 20- $\mu\text{m}$  thin films. To enable the replacement of hydrogen with deuterium in the case of thicker materials, we proceeded to the deuteration by synthesis: a deuterated MD (PTHF) or a deuterated CE (DEG) was chosen. The performance of these materials as elastomers was shown to vary greatly, depending on the composition and percentage of hydrogen bonding. For the materials obtained with the deuterated CE (DEG), we observed an increased resilience. The replacement of the normal PTHF by a deuterated PTHF soft-segment MD had no sensible effect of the mechanical response of the materials, both in the case of polymers with MDI and for those

with DBDI. However, regardless of the nature of the soft segment (normal or deuterated), the materials based on the couple DBDI–BG showed a higher input energy density and lower fractional energy recovery than did the corresponding MDI–DEG and DBDI–DEG based PUs.

In the case of the PUs achieved by partial replacement of the hydrogen with inert alchilic  $-\text{CH}_3$  groups, we observed a decrease of the stresses measured in the tensile tests and the molecular weight values expressed as the inherent viscosity. The total substitution of the hydrogen with  $-\text{CH}_3$  groups, resulted in a dramatic increase in the materials' inelasticity.

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