

Synthesis and Thermomechanical Characterization of Polyurethane Elastomers Extended with α,ω -Alkane Diols

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ABSTRACT: A series of polyurethane (PU) elastomers was prepared by the reaction of poly(ϵ -caprolactone) and 4,4'-diphenylmethane diisocyanate, which was extended with a series of chain extenders (CEs) having 2–10 methylene units in their structure. The completion of the reaction was confirmed by Fourier transform infrared spectroscopy. The chemical structures of the synthesized PU samples were characterized with Fourier transform infrared, ¹H-NMR, and ¹³C-NMR spectroscopy, and the thermal properties were determined by thermogravimetric analysis, DSC, and dynamic mechanical thermal analysis techniques. The mechanical properties were also studied and are discussed. The thermogravimetric analysis and DSC analysis showed that CE length had a considerable effect on the thermal properties of the prepared samples. The dynamic mechanical thermal analysis and damping peaks were also

affected by the number of methylene units in the CE length. The elastomer extended with 1,2-ethane diol exhibited optimum thermal properties, whereas the elastomer based on 1,10-decane diol displayed the worst thermal properties. Tensile strength and elongation at break decreased with increasing CE length, whereas hardness showed the opposite trend. The glass-transition temperature moved toward lower temperatures with increasing CE length. The decrease in the glass-transition temperature and tensile properties were interpreted in terms of decreasing hard segments and increasing chain flexibility. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1840–1849, 2008

Key words: elastomers; FT-IR; mechanical properties; polyurethanes; synthesis; thermal properties

INTRODUCTION

Polyurethane (PU) elastomers can be found in a variety of products that feature a range of properties and performance. This is a result of the extensive choice of chemicals that may be used in their synthesis. The majority of PU elastomers is, however, based on diisocyanates, long-chain components, such as polyesters and polyethers, and on short-chain difunctional (or multifunctional) alcohols or amines, which act as chain extenders (CEs). Because PU possesses various desirable properties, derived from its characteristic structure with phase separation from alternating hard and soft segments, it is widely applied in the fields of flexible fibers, paints, adhesives, artificial leather, and so on. PUs have a potential array of commercial applications as they can be molded, injected, extruded, and recycled.¹

From a generic point of view, it is accepted that better properties are achieved as the microphase segregation between the soft and hard blocks is

increased, and this morphology has been studied by spectroscopic, thermal, and microscopic techniques.^{2–6} The morphology of PU depends on the state of compatibility and microphase segregation between the two segments. The existence of the phase segregation caused by the clustering of hard and soft segments into separate domains has been a subject of continued research interest.^{7–9} Various polyols, diisocyanates, and CEs have been used in the synthesis of PUs, and their effect on the properties have been investigated.^{10–14} The structure of the CE has a significant effect on properties and morphology of the PU. A number of attempts have been made to improve the physical and thermal properties of PU. The physical and thermal properties of PUs have been varied by the variation of the formulation of PUs.^{8,15–22} Several studies have also reported that CE properties, such as the chain length, molecular volume, and functionality, can influence hard-segment packing and crystallinity in the hard domains.^{23–26} One factor, however, that strongly determines the CE chemical properties and molecular conformation is the chain length found within the CE backbone. First, it is important to consider that efficient packing in hard domains is

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largely driven by the amenability to strong hydrogen bonding between the hard segments of adjacent chains^{26,27} and that this can be affected by CE conformation.

In earlier research on CEs, Minoura et al.^{28,29} found that some particular combinations of low-molecular-weight diol and diisocyanate specifically affect the properties of elastomers. A characteristic odd–even dependence was observed when the mechanical properties of the elastomers were plotted against the number of methylene units. This effect was very pronounced in case of a lower number of methylene units. The difference in the packing and the dependence of the ability of intermolecular hydrogen-bonding tendency on the odd–even number of methylene units have also been investigated, discussed, and confirmed by X-ray diffraction. Ramesh et al.³⁰ compared the mechanical properties of several PUs made with different diamines or diols as the CE and found that the PU samples extended with diamines showed better properties than those extended with diols. The reason was that the increased intermolecular hydrogen bonding improved the aggregating strength. Martinez and Sanchez-Adsuar³¹ also compared the influence of various diols as CEs on the properties of the product and found that the chain length of the CE was able to affect the properties of the segment arranged structure and the character of the PU formed. Xiao et al.³² compared three CEs of different chain length and found that the longer the length of the CE was, the better were the mechanical properties of the resulting PU materials. Zawadzki and Akcelrud³³ observed that the values for the mechanical properties increased with decreasing number of carbon atoms in the CE, that is, 1,3-propane diol (PDO) > 1,4-butane diol (BDO) > 1,6-hexane diol (HDO). This finding disagreed with previous results, which showed a zigzag pattern²⁸ or an increase in properties with diol chain length.^{14,32}

Recently, Rogulska et al.³⁴ studied the effect of aliphatic–aromatic α,ω -diols as CEs on the properties of PU samples and reported that the mechanical properties were enhanced with the longest chain. They also found that all of these polymers showed very good thermal properties. Very recently, Azzam et al.³⁵ compared the effect of heterocyclic/aromatic diamine CEs with aliphatic diols and reported that the number of methylene units in the aliphatic diols did not affect the thermal stability of the PU samples. In their investigations, the Young's modulus and tensile strength were higher, whereas the elongation at break was lower, for the samples at room temperature. In the literature, none of the authors reported the effect of α,ω -alkane diols [1,2-ethane diol (EDO) to 1,10-decane diol (DDO)] to determine an exact picture of results with diol CEs.

From the aforementioned survey, it is very clear; the CE has a profound influence on the thermomechanical properties of the resulting PU through its aggregating function asserted between PU molecules. More over, a CE can be expected to bring in certain functional groups relevant to better thermomechanical properties. In our previous studies,^{36,37} we examined the effects of the structures of different types of CEs and diisocyanates on the thermal stability of PUs. In our investigations, the thermal stabilities were enhanced considerably with the addition of low-molar-mass diols used as CEs. However, the systematic study of the effect of the chemical structures of CEs and diisocyanates on the thermal stabilities of PUs was incomplete. In this project, a systematical explanation based on the study of the effect of α,ω -alkane diols (having methylene units of length 2–10) used as CEs on the properties of PUs was done to get a clear picture of the dependence of different mechanical and thermal properties on the number of methylene units in the CE.

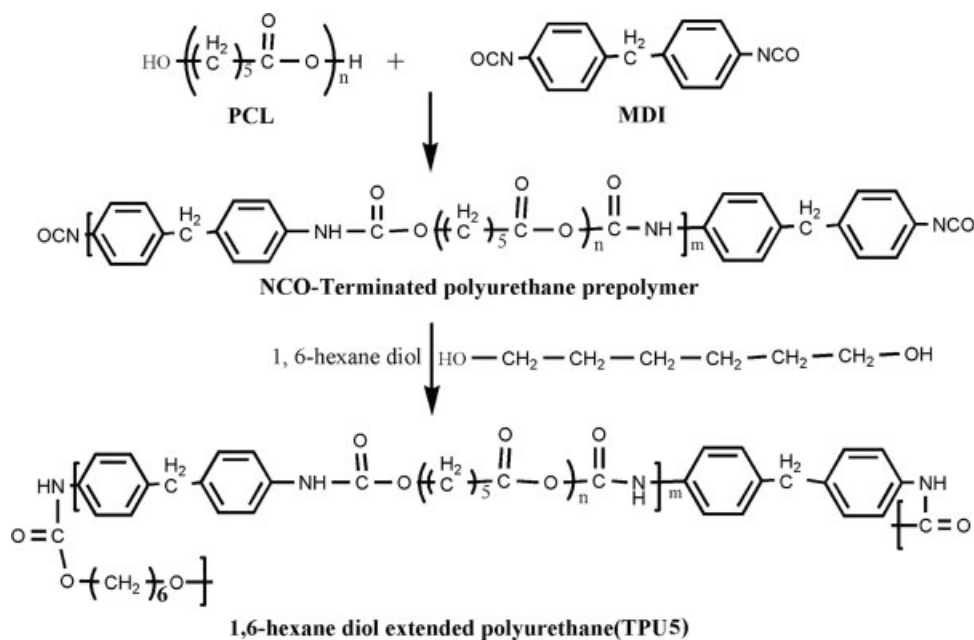
EXPERIMENTAL

Chemicals

4,4'-Diphenylmethane diisocyanate (MDI) was purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). The CEs [EDO, PDO, BDO, 1,5-pentane diol (P'DO), HDO, 1,8-octane diol (ODO), and DDO] were obtained from Merck Chemicals Co. (Darmstadt, Germany) Polycaprolactone diol, CAPA 225 (molecular weight = 2000, Solvay Chemicals, Cashur, England), and all the CEs used in this study were dried at 80°C *in vacuo* for 24 h before use to ensure the removal of all air bubbles and water vapors that may otherwise have interfered with the isocyanate reactions. The molecular weight of CAPA 225 was confirmed by the application of the procedure reported in ASTM D 4274C.³⁸ MDI and all of the other materials were used as received. All of the reagents used in this study were analytical grade.

Synthesis of the polymer (PU)

For this investigation, a prepolymer was synthesized, as given in our previous studies,^{36,37} by the step-growth polymerization of poly(ϵ -caprolactone) (PCL) and MDI and extended with series of CEs (Scheme 1). Into a four-necked reaction kettle equipped with a mechanical stirrer, heating oil bath, reflux condenser, dropping funnel, and N₂ inlet and outlet was placed PCL (31.25 g, 0.0156 mol). The temperature of the oil bath was increased to 60°C. Then, MDI (11.95 g, 0.047 mol) was added, and the temperature was increased to 100°C. It almost took 1.0 h to obtain the NCO-terminated prepolymer. A Fourier transform infrared (FTIR) spectrum of the prepolymer was



Scheme 1 Chemical route for the synthesis of PU elastomers.

obtained to monitor the prepolymer reaction (Fig. 1). We carried out the conversion of the prepolymer into the final PU by stirring the prepolymer vigorously and then adding a previously degassed CE, such as HDO (3.69 g, 0.0313 mol). By the progress of the reaction, the uniphase behavior of the reaction mixture indicated the completion of the reaction, and the liquid polymer was cast into a mold of Teflon plates to form a uniform sheet 2–3 mm thick. The synthesized polymer was first placed *in vacuo* for 15 min to ensure the removal of air bubbles before casting and then cured for 24 h in a hot-air circulating oven at 100°C. Before testing, the cured sample sheets were then stored for 1 week at ambient temperature (25°C) and 40% relative humidity.

The procedures for prepolymer synthesis and film casting were the same as those described briefly in the synthesis of TPU5 (HDO). For each sample, the prepolymer was extended with a weighed amount of alkane diol CE (0.0313 mol), as given in Table I. All other parameters and the temperature condition remained same as described previously in the synthesis of TPU5. A schematic illustration of the synthesis of the HDO-based PU (TPU5) is shown in Scheme 1.

Measurements

Infrared measurements were performed on a Bruker (Ettlingen, Germany) IFS 48 FTIR spectrometer. The ¹H-NMR and ¹³C-NMR spectra were recorded in a deuterated dimethyl sulfoxide (DMSO-*d*₆) solution with a Bruker Advance 400-MHz spectrometer. Chemical shift (δ) values were given in parts per million with tetramethylsilane as a standard. The

thermal history was recorded with differential scanning calorimetry (DSC; Stanton Redcraft STA-780, London). Thermogravimetric analysis (TGA) was done on a Polymer Lab TGA-1500 instrument (London) under a N₂ atmosphere from room temperature up to 600°C at a heating rate of 20°C/min. The dynamic mechanical measurements were performed on a UK Polymer Lab dynamic mechanical thermal analyzer (model MK-II, Polymer Laboratories, Loughborough, UK) over a temperature range of –150°C to 200°C at heating rate of 10°C/min and a frequency of 1 Hz. The dimensions of samples were

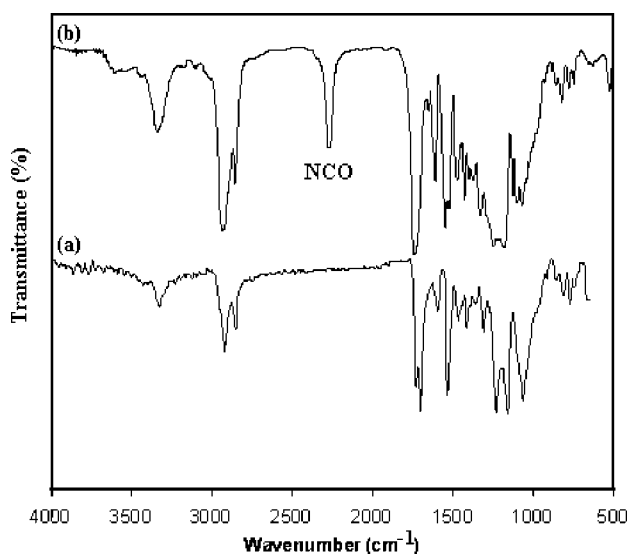


Figure 1 FTIR spectra of (a) the PU film and (b) the PU prepolymer.

TABLE I
Sample Code Designations and Different Formulations of PUs

Sample number	Sample code	CE	CAPA225 : MDI : CE molar ratio (mass)
01	TPU1	EDO	0.0156 mol (31.25 g) : 0.047 mol (11.95 g) : 0.0313 mol (1.94 g)
02	TPU2	PDO	0.0156 mol (31.25 g) : 0.047 mol (11.95 g) : 0.0313 mol (2.38 g)
03	TPU3	BDO	0.0156 mol (31.25 g) : 0.047 mol (11.95 g) : 0.0313 mol (2.82 g)
04	TPU4	P'DO	0.0156 mol (31.25 g) : 0.047 mol (11.95 g) : 0.0313 mol (3.24 g)
05	TPU5	HDO	0.0156 mol (31.25 g) : 0.047 mol (11.95 g) : 0.0313 mol (3.70 g)
06	TPU6	ODO	0.0156 mol (31.25 g) : 0.047 mol (11.95 g) : 0.0313 mol (4.14 g)
07	TPU7	DDO	0.0156 mol (31.25 g) : 0.047 mol (11.95 g) : 0.0313 mol (5.44 g)

30 × 10 × 1 mm. The values of the loss tangent ($\tan \delta$) and storage modulus versus temperature were recorded for each sample. The mechanical properties, including tensile strength and elongation at break, were determined from the stress-strain curves with an MTS (MTS System Corporation, Eden Prairie, MN) tensile tester model 10/M at a strain rate of 50 mm/min. The measurements were performed at 25°C with a film thickness of about 1 mm, and the films were stamped out with an ASTM D 638 die.³⁸ The hardness of the PU samples was measured by a Zwick instrument (Ulm, Germany) in Shore A scale.

RESULTS AND DISCUSSION

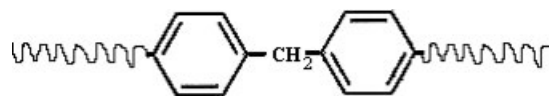
The main aim of this research was to study the effect of α,ω -alkane diols on the thermal and mechanical properties of PU elastomers. So, the synthesis of these PU elastomers based on different diols was performed according to Scheme 1. The reaction of 1 equiv of polyol with 3 equiv of MDI led to an NCO-terminated PU prepolymer, which was subsequently extended with 2 equiv of CE to prepare final PU.

Molecular characterization

We verified the completion of the polymerization reaction by an FTIR technique by monitoring the disappearance of the peak at 2265 cm^{-1} (ν NCO). The FTIR spectra of the PU prepolymer and the cast films that we obtained are shown in Figure 1. The observed peaks in the spectrum confirmed that the reaction was completed and that the predesigned PU was formed. The FTIR spectra of the samples also supported the proposed structure of the final polymers. The FTIR spectra showed characteristic bands of urethane groups at 3330 cm^{-1} (N—H stretching). The other peaks (cm^{-1}) observed were assigned as follows: 2947 (C—H symmetric stretching vibrations of CH_2); 2810 (C—H asymmetric stretching vibrations of CH_2 groups); 1728, 1642 (C=O bond); 1599, 1529 (N—H deformations); 1464 (CH_2 bending vibration); 1407 (C—H bending vibration); 1311 (CH_2

wagging). Peaks corresponding to the absorption of —NH, —CO, —CHN were observed at 3330, 1728, and 1464 cm^{-1} , respectively, which indicated the synthesis of a product having —NHCOO groups. The observed N—H bending vibrations at 1529 cm^{-1} (C—O—C stretching absorption band corresponding to the ether oxygen of the soft segment at 1000–1150 cm^{-1}) also provided strong evidence for the formation of PU.

The $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) and $^{13}\text{C-NMR}$ (400 MHz, $\text{DMSO-}d_6$) spectra of the final synthesized PU samples (TPU1–TPU7) were in accordance with the proposed structures. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of PU extended with PDO (TPU2) are shown in Figure 2(a,b). The signal of urethane (NH) was observed at 8.46 ppm, and the peaks observed at 7.05–7.45 ppm were assignable to aromatic protons. Some other peaks at 1.29–4.08 ppm, assignable to the protons of CH_2 and CH_2OCO , supported the formation of PU. In the $^1\text{H-NMR}$ spectra [Fig. 2(a)], observed peaks (ppm) were assigned as follows: 8.46 (s, NH); 7.3–7.2 (m, 4H); 7.08–7.02 (m, 4H); 4.05–3.93 (broad, 4H); 3.77–3.73 (s, 2H); 3.36 (m, 2H); 2.47 (DMSO); 2.21 (m, 2H); 1.48–1.35 (m, 2H); 1.34–1.24 (m, 2H). For the $^{13}\text{C-NMR}$ spectra [Fig. 2(b)], observed peaks (ppm) were assigned as follows: 173.2, 173.1, 154.8 (C=O); 137.6, 135.9, (aromatic C); 129.2, 118.7 (aromatic CH); 64.4, 63.9, 61.0, 40.7, 40.6, 40.4, 40.1, 39.9, 39.7, 39.5, 39.3, 34.9, 33.8, 28.9, 25.5, 25.4, 24.6, 25.5 (CH_2). In the $^{13}\text{C-NMR}$ spectra of the final PU samples, we observed that the peak located at 40 ppm presented a progressive intensity increase. This result was attributed to the overlapping of — CH_2 — signals with those due to the aromatic chemical structure:



Thermal characterization

TGA and DSC analysis

The TGA technique was used to evaluate thermal stability of the prepared polymers. The results are reported in Table II. The TGA curves of the samples

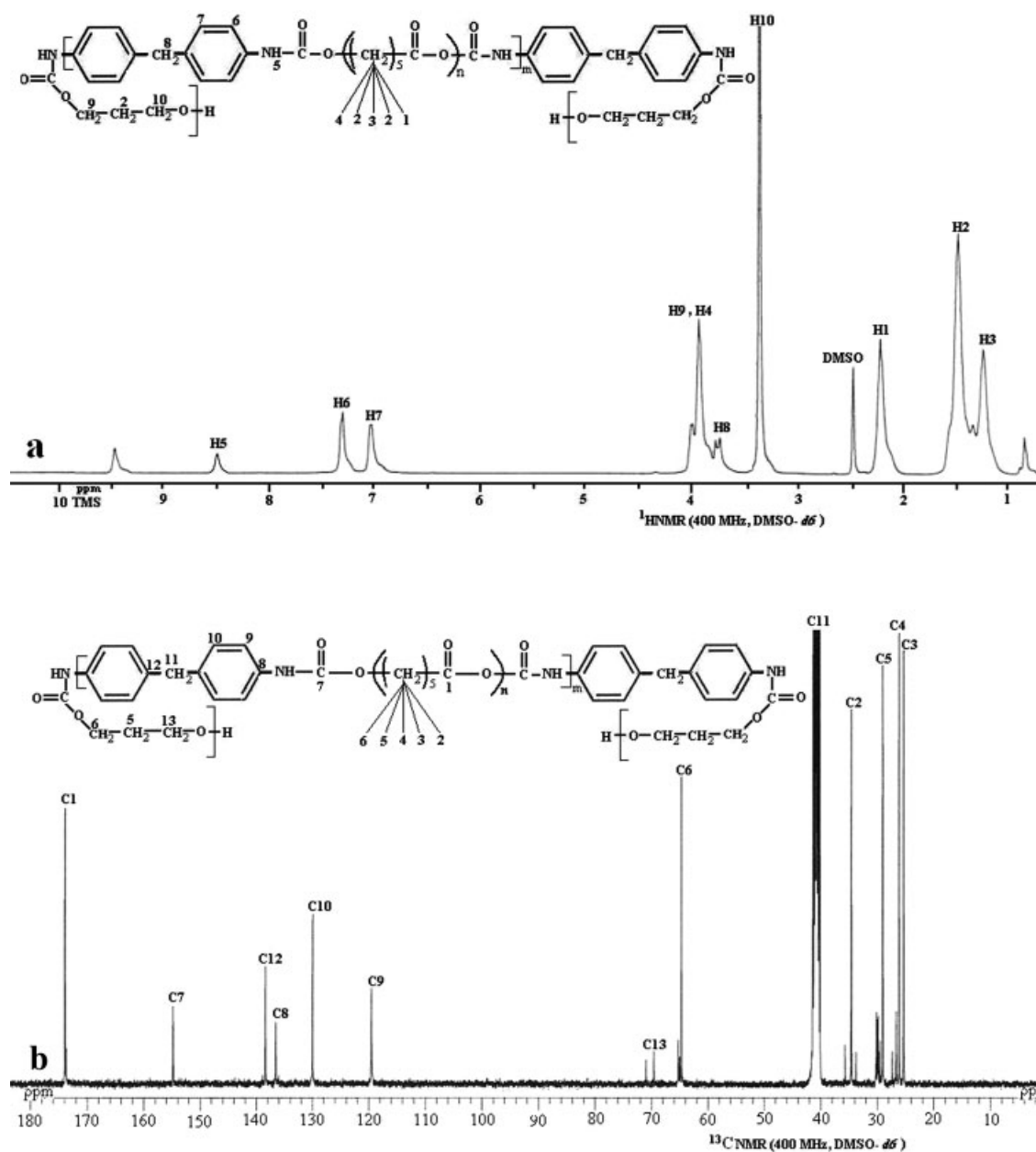


Figure 2 (a) ¹H NMR and (b) ¹³C NMR spectra of PU extended with 1,3-propane diol (TPU2).

as a function of CE length are shown in Figure 3. For the prepared final PU, the decomposition temperature for 10% weight loss was in the range 290–325°C. The maximum decomposition temperature was in the range 582–604°C. It was quite clear that a sample extended with EDO (TPU1) was thermally more stable than all of the other samples. We observed that an increase in the CE length decreased the thermal stability of the PU films. This meant that the number of methylene units in the aliphatic diols used as CEs had a considerable effect on the thermal stability of the prepared PU samples. We can successfully state that the early stage degradation

occurred mainly in the hard segments where urethane groups first underwent depolymerization, which resulted in individual monomers, and then, their further reaction produced carbon dioxide.³⁹ TGA studies of the PU films showed that the degradation of PU films started at about 300°C and ended at 600°C. The degradation at 600°C corresponded to the formation of char. We concluded that an increase in CE length resulted in a decrease in the thermal stability of the final PU. This lower thermal stability was probably due to the significantly lower MDI mass fraction and, therefore, a lower interurethane H-bonding tendency. We considered that an increase

TABLE II
Thermal Stability and Dynamic Mechanical Analysis Data of the Samples

Sample number	Sample code	T_{10} (°C)	T_{20} (°C)	T_{50} (°C)	T_{\max} (°C)	T_g (°C) ^a	Tan δ ^b
01	TPU1	325	340	374	604	-22.5	0.94
02	TPU2	312	335	370	594	-29.7	0.73
03	TPU3	310	322	349	595	-30.8	0.59
04	TPU4	307	324	368	595	-31.5	0.62
05	TPU5	305	320	351	603	-36.3	0.42
06	TPU6	298	318	346	592	-37.3	0.37
07	TPU7	290	315	340	582	-39.5	0.34

T_{10} , T_{20} , and T_{50} are the temperatures of 10, 20, and 50% weight losses, respectively, obtained from TGA; and T_{\max} is the maximum decomposition temperature obtained from TGA.

^a The center of the tan δ peak was used for the determination of T_g .

^b The altitude of the tan δ peak.

in the CE length diluted the urethane linkages, which resulted in a lower interurethane H-bond concentration.

The effect of CE length on the structure of the PU samples was studied by DSC measurements. For instance, the DSC thermograms of the PU extended with a series of CEs are shown in Figure 4. From Figure 4, it is clear that all the PU samples had degraded partially at temperatures above 300°C, and this degradation temperature was also confirmed by TGA data (Table II). Moreover, the peak observed at a temperature of about 315°C became clearer and bigger with increasing CE length in the PU backbone and shifted to a higher temperature. The shift of the peak from 315°C and the corresponding area under

the peak strengthened the concept of the conformational freedom and packing of the hard segment. With increasing CE length, the conformational freedom for the packing of the hard segment increased, which led better packing of the hard segment. We clearly observed that an increase in the number of methylene units resulted in an increase in better phase separation between the hard and soft segments, which was also evident from the DSC peak becoming more clear and significant in melting region of the polymer. On the other hand, the peak located at 405°C became smaller and seemed to disappear, without changing its position, with increasing CE length. This behavior may have been due to the fact that an increase in CE length resulted in a

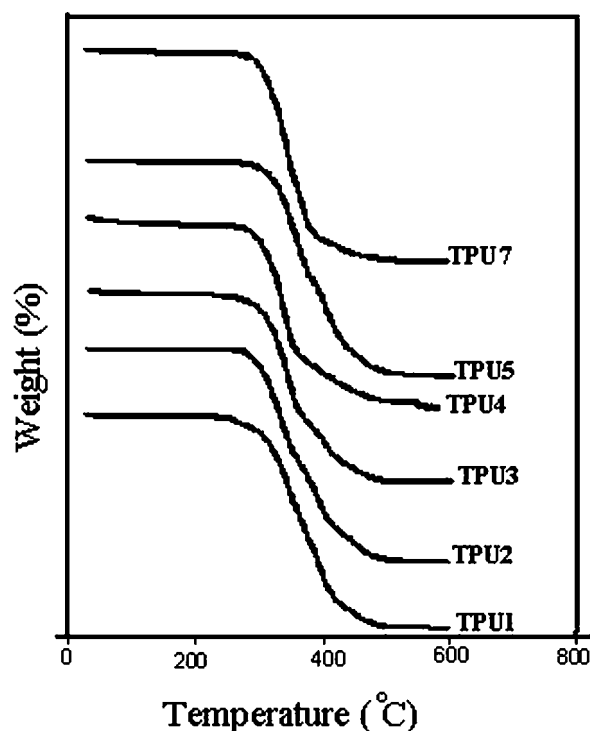


Figure 3 TGA thermograms of PUs.

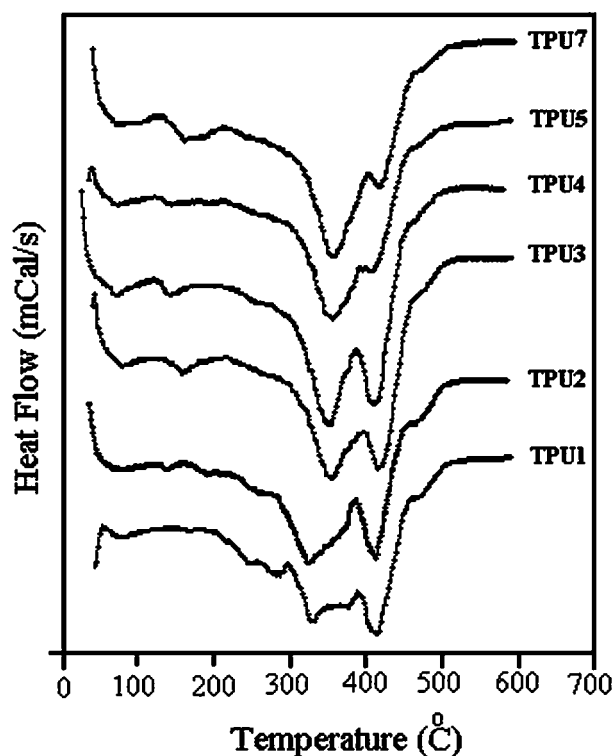


Figure 4 DSC measurements of PUs.

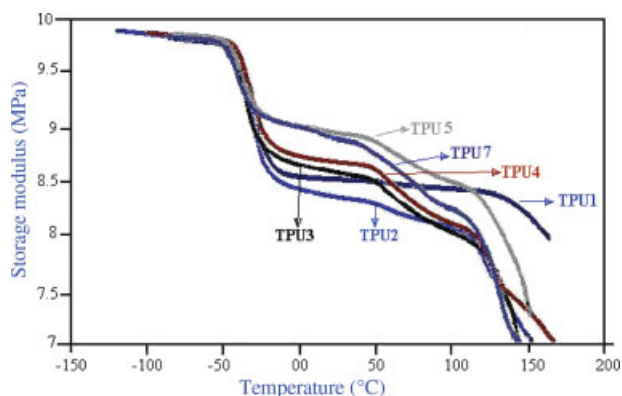


Figure 5 Storage modulus/temperature curves of PU samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

decrease in the NH content, which ultimately led to a decrease in H bonding. Less H bonding resulted in a lower thermal stability. If H bonding was within the hard segment, the final PU had a better thermal stability than a PU with H bonding between the hard segment and the soft segment. Therefore, thermal degradation peak located at about 405°C (TPU1) became smaller and disappeared to indicate that the final PU sample extended with DDO (TPU7) was degraded at 355°C. We concluded that CE length had a considerable effect on the thermal degradation of PU, and when the CE length was increased, the thermal degradation shifted to lower temperatures, as is obvious from Figure 4.

Dynamic mechanical thermal analysis (DMTA) studies

DMTA was used to study the viscoelastic properties of the prepared samples. DMTA allows different types of transitions and relaxations to be detected and related to the structure and morphology of samples. The data of thermal transition is collected in Table II, and the storage modulus and $\tan \delta$ values as functions of temperature are shown in Figures 5 and 6. The determination of the storage modulus of the prepared samples was helpful in determining the nature of the final samples, whether it was stiff or elastic. It is obvious from Figure 5 that any increase in the CE length resulted in a change in the thermal transition behavior of the final PU. Also, PU extended with EDO (TPU1) had an obviously higher plateau modulus and wider plateau temperature range than all of the other samples. This suggested that the molecular rigidity of TPU1 was higher than that of all of the other samples, which could have played a significant role in the determination of the physical properties. The plateau modulus continuously decreased with increasing number of methyl-

ene units in the CE. This behavior implied that the MDI ratio used to establish the prepolymer remained the same for the whole study whether we extended the prepolymer with EDO, PDO, or DDO. As we increased the CE length, the MDI mass fraction led to a decrease and resulted in a decrease in the interurethane H-bond concentration. This decrease in H-bond concentration also decreased the storage modulus of the polymer sample. In comparison with TPU7, TPU1 showed a much higher plateau modulus with a wider plateau temperature range than TPU7. This suggested that the strength and heat resistance of PU decreased with increasing number of methylene units in the PU backbone. It was possible to use the sample TPU1 in a wide range of temperatures without sacrificing the properties. Below the glass-transition temperature (T_g), all of the samples had almost the same storage modulus. Once T_g was reached, the modulus began to decrease rapidly. The modulus for sample TPU7, with a higher crystallinity, decreased at a faster rate than the sample TPU1, with a lower crystallinity.⁴⁰ We concluded that by increasing the CE length in the PU formulation, the stiffness of the samples decreased, and this behavior was strongly supported by the DMTA study. It is thought that the degree of crystallinity (W_c) and molecular orientation are affected by heat treatment and stress in polymer processes. These structural changes have profound effects on the dynamic mechanical properties.

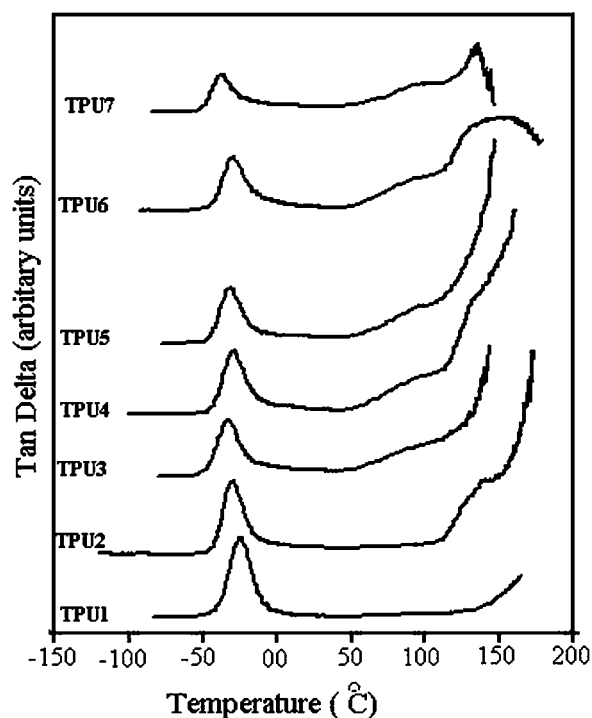


Figure 6 $\tan \delta$ /temperature curves of PU samples.

TABLE III
Mechanical Property Data of the PU Samples

Sample number	Sample code	Tensile strength (MPa)	Elongation at break (%)	Hardness
1	TPU1	29.59	257.79	76.98
2	TPU2	25.36	255.13	73.66
3	TPU3	22.01	249.64	76.02
4	TPU4	18.14	246.63	77.70
5	TPU5	16.64	245.69	79.86
6	TPU6	14.51	243.24	79.77
7	TPU7	12.27	241.05	80.04

The investigation of the $\tan \delta$ curves (Fig. 6) showed that in the $\tan \delta$ peaks for all of the samples, the glass transition occurred within a broader temperature range. The increase in CE length resulted in a decrease in both the intensity and broadening of the peaks (Fig. 6). This broadening was attributed to an increase in the distribution of molecular weight. It is well known that T_g is affected by a number of chemical and molecular structures. The flexibility of the molecular chain, the bulkiness of the side groups attached to the backbone, and molecular polarity affect T_g of the samples. The damping peak ($\tan \delta$ peak) height and the temperature at which the α -peak occur are closely related to the glass-transition phenomenon. Therefore, similar interpretation was used to determine the T_g of the prepared samples through the center of the damping peaks. An increase in the CE length resulted in a decrease in the damping peak intensity. This decrease in damping peak intensity resulted in a decrease in the energy dissipation of the polymers. T_g of PU ($\tan \delta$) moved toward lower temperatures as the CE length increased. The $\tan \delta$ peak located at about -22.5°C shifted to about -39.5°C as the number of methylene units increased. This decrease in T_g with increasing CE length was mainly due to increased chain flexibility in the PU structure (Fig. 6 and Table II). Moreover, the amplitude of the $\tan \delta$ peak became smaller as the CE length increased. This phenomenon was attributed to the increase in the crystallinity of the samples in accordance with the increase in CE length. It has also been previously reported that the intensity of the damping peak ($\tan \delta$) decreases with increasing W_C of the PU sample. Usually, $\tan \delta$ is given by the following equation:⁴¹

$$\tan \delta = W_C(\tan \delta)_c + (1 - W_C)(\tan \delta)_a \quad (1)$$

where subscripts a and c refer to the contributions of the amorphous and pure crystalline phases, respectively. Because $\tan \delta$, in general, is mostly due to the amorphous phase, the $\tan \delta$ equation for the maximum in the $\tan \delta$ peak can be simplified as

$$\tan \delta \cong (1 - W_C)(\tan \delta)_a \quad (2)$$

This equation shows that $\tan \delta$ decreases with increasing W_C , and the same trend was observed in this study.

Mechanical property studies

Tensile behavior in mechanical testing is commonly expressed by stress–strain curves. The types of these curves indicate whether materials are hard, brittle, tough, ductile, and/or soft. The mechanical parameters of the samples are summarized in Table III. The sample TPU1 (PU extended with EDO) showed a significantly higher tensile strength and breaking strain than all of the other samples. This behavior was attributed due to the increased intermolecular forces associated with the TPU1 sample. It may also have been due to higher hard-segment contents for the same NCO/OH ratio and the highest hydrogen-bonding density. All of the samples displayed a smooth transition in the stress–strain behavior from the plastic to the elastic deformation region as the CE length increased. Comparison of the whole mechanical properties data of samples showed that samples containing a lower number of methylene units had higher strengths than those containing higher ones. These results did not agree with the previous results, which showed a zigzag pattern²⁸ or an increase in properties with diol chain length.^{14,32} The former behavior was explained in terms of the number of hydrogen bonds that could be formed for each repeating unit of the hard segment, which was two for even-numbered CEs and one for odd-numbered CEs. In fact, this explanation presumes a perfectly ordered arrangement within the hard domains, which did not hold for the PUs in our case. In previous studies,^{14,32} the increase in ultimate stress and 50% modulus with diol chain length found for dimeryl diisocyanate, hexamethylene diisocyanate, and cyclohexyl diisocyanate PUs extended with aliphatic diols was attributed to an increase in compatibility for the hydroxy-terminated polybutadiene

(HTPB)–diol system with the diol chain length. Greater amounts of the diol were then be able to copolymerize with the HTPB through the diisocyanate, which resulted in increasing concentrations of urethane groups in the HTPB matrix, which thus provided a higher mechanical strength. The mechanical properties depended not only on the phase separation but also on the hydrogen bonding. A decrease in hydrogen bonding resulted in a decrease in the mechanical properties. With increasing CE length, the NH content per unit volume of PU decreased and, ultimately, showed a decrease in hydrogen bonding and the mechanical properties of the PU. In a comparison of TPU1 and TPU7, TPU1 showed a higher tensile strength than TPU7. We concluded that the strength of the PUs was decreased with increasing CE length in the PU backbone. This decrease in the tensile properties was a result of a decrease in the cohesive forces of the PU structure.

The hardness data of the samples are also collected in Table III. The hardness of the PU samples increased with increasing number of methylene units. In a comparison of TPU1 and TPU5, the latter showed more hardness than the former. We concluded that the hardness of the polymers increased as the CE length increased. Many researchers have predicted that hardness is an indication of the storage modulus; however, in this study, we obtained inverse results. It is a well-established phenomenon that T_g is related to the amorphous region, which is in this case, depended on the conformational behavior of the soft segments. So, the higher the conformational freedom in the soft segments was, the lower the T_g of the materials should have been, which was clear from the DMTA studies. When we observed the material properties well above T_g , the main controlling factor of the properties of the material was the nature and degree of orientation in the ordered region of the material. At room temperature, which was higher than T_g , the ordering of the hard segments was more obvious with a higher number of methylene units (C atoms). This ordering could be the valid reason for the observation of the relatively mild changes in the hardness of the material.

CONCLUSIONS

PU elastomers based on MDI and PCL and extended with a series of CEs were synthesized via a two-step polymerization technique. The effect of CE length on the thermal and mechanical properties was studied. The TGA and DSC analysis of these samples showed that CE length had a considerable effect on the thermal properties of the prepared samples. DMTA and damping peaks were also affected by the number of

methylene units in the CE length. Tensile strength and elongation-at-break decreased with increasing CE length, whereas hardness increased. T_g moved toward lower temperatures with increasing CE length. The decreases in T_g and the tensile properties were interpreted in terms of decreasing hard segments and increasing chain flexibility and phase separation. Finally, the decrease in the thermal and mechanical properties was interpreted in terms of decreasing MDI mass fraction and lower interurethane H-bonding concentration as the CE length increased.

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