

Synthesis and Characterization of New Polyurethane Based on Polycaprolactone

El Miloud Maafi,^{1,2} Fouad Malek,¹ Lan Tighzert²

¹Laboratoire de Chimie Organique Macromoléculaire et Produits Naturels, Faculté des Sciences, Université Mohamed Premier, Bd Mohamed VI, BP 717, Oujda 60000, Maroc

²Groupe de Recherche En Sciences Pour l'Ingénieur, Laboratoire d'Etudes des Matériaux Polymères d'Emballage (GRESPI/LEMPE—EA 4301), Ecole Supérieure d'Ingénieurs en Emballage et Conditionnement (ESIEC), Esplanade Roland Garros, Pôle Henri-Farman, B.P.1029—51686 Reims Cedex 2, France

Received 20 May 2009; accepted 11 September 2009

DOI 10.1002/app.31448

Published online 4 November 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Different polyurethane (PU) were synthesized from ϵ -polycaprolactone diol, 4,4'-diphenyl methane diisocyanate (MDI) and bis(2-hydroxyethyl)terephthalate (BHET), using a two-step method and a one-step method providing regular and random distributions of starting monomers in the PU chains. Even with an identical molar monomer composition, the properties of obtained PU are different depending on the method of synthesis. The structure of PU

was characterized by ¹H and ¹³C-NMR and Fourier transform infrared spectroscopy (FTIR). The thermomechanical properties of synthesized PU were also studied demonstrating the influence of aromatic ring in the macromolecular chain. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3651–3658, 2010

Key words: polyurethane; polycaprolactone; polycondensation; thermomechanical properties

INTRODUCTION

The development of biodegradable polyurethanes (PUs) has drawn much attention last two decades for their excellent physical properties, their biocompatibility and biodegradability.^{1–8} These materials are mainly used in biomedical field as the suture yards,^{9,10} controlled release systems of active ingredients,^{11,12} implants for orthopaedic surgery^{13,14} and in tissue engineering.^{14,15}

PU materials are composed of flexible segments and rigid segments. The flexible and soft segment is usually an amorphous prepolymer diol of molecular weight relatively high. The rigid segment is composed of a diisocyanate and a diol, and both have low molecular weight. The composition or the ratio of flexible to rigid segments lends a wide range of physical properties to PU materials. Many authors^{16–21} have studied the morphology, the thermal and mechanical properties, the permeability of PUs and their biodegradability depending on their composition in flexible and hard segments, the nature and the mo-

lecular weight of the flexible segment, as well as their synthesis method.

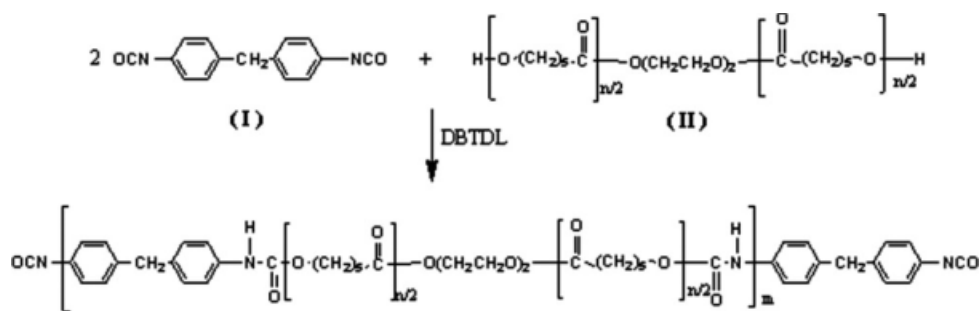
The biodegradable PU are synthesized by incorporating flexible segments which are able to be hydrolyzed, such as poly(ϵ -caprolactone) (PCL), poly(lactide), poly(glycolide), and poly(alkyl adipate).^{1–15} The PU based on PCL has been widely studied. Indeed, PCL is a linear aliphatic polyester, semicrystalline, hydrophobic, biocompatible, bioresorbable, and biodegradable. Moreover, it is characterized by a degradation time *in vivo* which is remarkably long compared to polylactide. In addition, PCL has a very light inflammatory response with tissue.²²

PCL is also interesting in the field of environment, especially in the packaging. However, the latter application remains restricted because PCL suffers from a number of disadvantages, notably a limited service temperature induced by its low melting temperature and a low Young's modulus.

According to the literature,^{23–26} the introduction of terephthalic units (TU%) in the structure of polyesters improves their physical properties. The poly(butylene adipate-co-terephthalate) is one of the copolyesters which has been widely studied and marketed under the name of Ecoflex[®]. Witt et al.²⁴ have shown that this copolyester has good mechanical and thermal properties when the molar concentration of terephthalic acid is superior to 25%, but its rate of biodegradation declines sharply at a concentration higher than 50%. Therefore, the ratio of aliphatic and aromatic units must be chosen

Correspondence to: L. Tighzert (lan.tighzert@univ-reims.fr).

Contract grant sponsor: Franco-Moroccan Mixed Committee; contract grant number: MA/07/176.



Scheme 1 Structure of prepolymer obtained by reaction of a diisocyanate (MDI) and a diol (PCL).

judiciously for syntheses. For a terephthalic acid molar concentration between 25 and 50%, the copolyesters reach a good compromise between biodegradability and properties of use.

In this study we planned to synthesize new polycondensates based on PCL. Their structure contains urethane groups and aromatic rigid segments in limited quantities to preserve the polymer biodegradability. For these syntheses, 4,4'-diphenylmethane diisocyanate (MDI) and bis(2-hydroxyethyl) terephthalate (BHET) as a chain extender will be used. Different molar ratios of the initial mixture [dihydroxy oligomers]/[diisocyanate] will be studied. These conditions enable us to obtain PUs with different structures and properties. This article describes different synthesized PUs and their thermal, mechanical and wetting properties.

EXPERIMENTAL

Materials and syntheses

Reagents

PCL diol (2000 g/mol), 2-hydroxyethyl terephthalate (BHET) were supplied by Aldrich and kept in a vacuum desiccator in the presence of P_2O_5 . 4,4'-diphenylmethane diisocyanate (MDI), tetrahydrofuran (analysis grade) (THF) and chloroform (analysis grade) ($CHCl_3$) were also purchased from Aldrich. MDI might dimerize at room temperature, therefore it was stored in a refrigerator at $-10^\circ C$.

Two-step synthesis of segmented polyurethane PUo

In a 250 mL reactor, equipped with a mechanical agitation and a supply of nitrogen, 20 g (0.01 mol) of PCL, 5.26 g (0.021 mol) of MDI and 15 mL of THF were simultaneously introduced. The mixture was heated at $60^\circ C$ for 2 h.

In the second stage, a solution of 2.54 g (0.01 mol) of BHET in 10 mL of THF was added. The mixture was then heated at $60^\circ C$ for 3 h. THF was removed by heating at $80^\circ C$. A solid PU was obtained and PU films were prepared by casting using chloroform as a solvent.

One-step synthesis of random polyurethane PUi

In a 250 mL reactor, equipped with a mechanical agitation and a supply of nitrogen, PCL, BHET, MDI solubilized in 20 mL of THF were simultaneously introduced. The mixture was heated at $60^\circ C$ for 5 h. THF was then removed by heating at $80^\circ C$. PU films were prepared by casting using chloroform as a solvent.

Preparation of films by casting

In a beaker, 10 g of PU to 50 mL of chloroform was introduced. After complete polymer solubilization, the solution was poured into a petri dish. The solvent was evaporated at $30^\circ C$ for 2 h. PU films were dried under vacuum for 48 h.

Techniques

Fourier transform infrared spectroscopy

The fourier transform infrared spectroscopy (FTIR) spectra were recorded on an FTIR 8400 SHIMADZU between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} . Samples were in film form. The number of scans was 20 for each sample.

Nuclear magnetic resonance

The 1H and ^{13}C -NMR spectra were recorded on a Bruker spectrometer Spectrospin 250 MHz. The solvent used was $CDCl_3$. Chemical shifts are given in ppm relative to Tetramethylsilane (TMS) as an internal reference.

Size exclusion chromatography

The size exclusion chromatograms (SEC) were recorded on an IOTA2 equipped with a Jasco PU-980 Intelligent HPLC pump and a column PLgel 5 μm MIXED-D $300 \times 7-5\text{ mm}$ (VARIAN INC). The eluent phase was chloroform and the flow rate was 1 mL/min. Samples were injected using an injector of the Agilent 100 Series. Molar masses were determined by using monodisperse polystyrene standards.

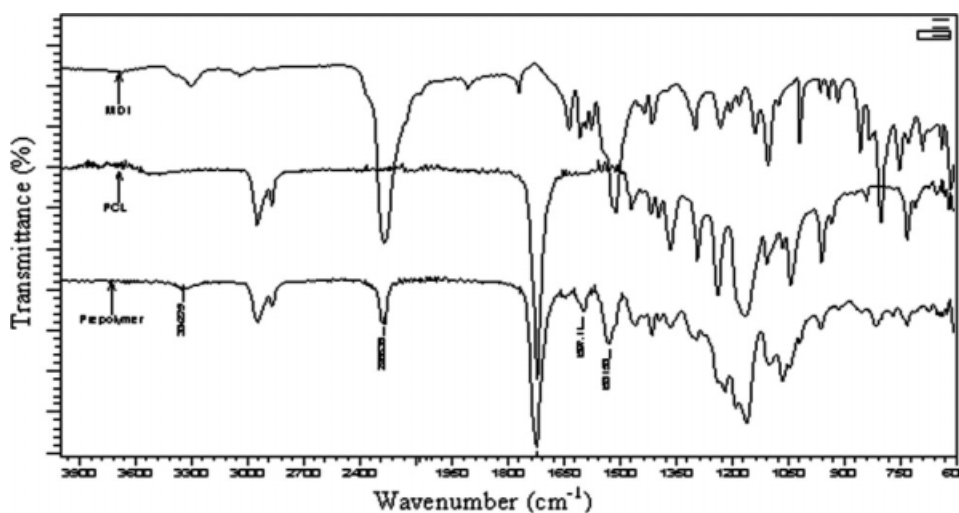


Figure 1 FTIR spectrum of reagents and prepolymer obtained by reaction of a diisocyanate (MDI) and a diol (PCL).

Differential scanning calorimetry

The Differential scanning calorimetry (DSC) analyses were performed with a 204 F1 NETZSCH apparatus. Experiments were carried out under nitrogen with samples ranging from 15 to 20 mg. A heating scan was conducted from -80 to 250°C with a heating rate of 10 K/min . Glass transition temperature was taken as the midpoint of heat capacity change.

Contact angle measurements

Contact angles were measured on a Dataphysics—Contact Angle System OCA. A drop of water was deposited on films. The contact angle θ_i was measured after stabilization of the drop spreading by means of a camera connected to a software image analysis. The contact angle values were obtained from the average of tests on 10 drops.

Mechanical properties

Mechanical tests were carried out with a machine of type MTS Adamel Lhomargy-DY35XL equipped with a load cell of 500N on shaped dumbbell type

H3 samples (ISO 37, 34 mm of length, and 4 mm of width). Tensile speed was 10 mm/min , at room temperature. The curves obtained enabled us to access the Young's modulus, tensile strength and elongation at break. For each sample, mechanical properties were obtained from the average of tests on 10 specimens.

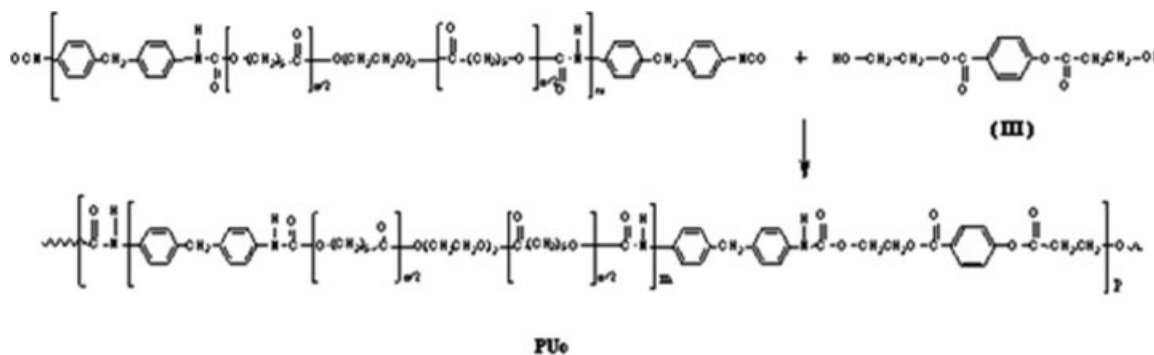
RESULTS AND DISCUSSION

Preparation and characterization of PU films

Two-step synthesis of segmented polyurethane PUo

To control the distribution of PCL and BHET along the polymer chain, a segmented PUo was initially synthesized by the method of prepolymers. The first step in this synthesis was the condensation between the α,ω -dihydroxy oligomers of PCL and MDI (Scheme 1). The initial molar reagent ratio $[\text{MDI}]/[\text{PCL}]$ was 2.1. The excess of MDI enables a prepolymer with NCO groups at both chain ends to be obtained.

The FTIR spectrum of PU prepolymer obtained (Fig. 1) clearly shows the formation of urethane



Scheme 2 Structure of prepolymer extended with BHET diol.

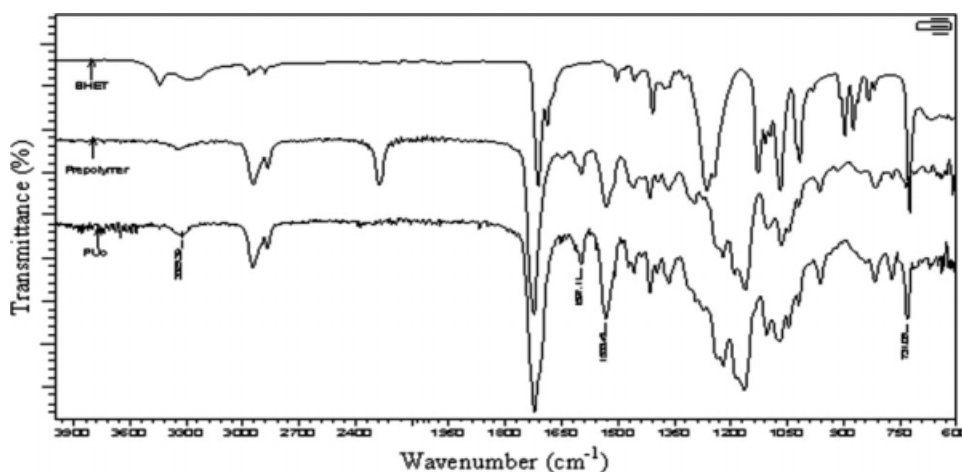


Figure 2 FTIR spectrum of prepolymer, BHET and PUo.

groups by the presence of absorption bands at 3342 and 1531 cm^{-1} due to elongation and deformation vibrations of $N-H$ bond, respectively. The presence of the absorption band at 1724 cm^{-1} , characteristic of the valence vibration of $C=O$ bond in urethane groups and ester groups is also noticed. Moreover, the band at 1597 cm^{-1} characterizes the aromatic ring vibration. FTIR analysis also reveals the presence of a band at 2268 cm^{-1} corresponding to the isocyanate function. These results confirm that NCO terminated PU prepolymers have been obtained.

In second step, BHET was used as a chain extender (Scheme 2). At the time when BHET was added, the solution became slightly cloudy, probably

due to a segregation phase in the material relating to soft and hard domains.²¹

On the FTIR spectrum of PUo (Fig. 2), the characteristic band of isocyanate group at 2268 cm^{-1} completely disappears. This fact affirms that the chain extension was complete. Besides, the appearance of an intense band at 3325 cm^{-1} characteristic of valence vibration of bound $N-H$ linkage and a band at 731 cm^{-1} characteristic of aromatic $C-H$ linkage deformation is clearly observed. These results confirm that the PUo synthesis was successful and the chemical structure of PU is well that expected.

In Figures 3 and 4, ^1H and ^{13}C -NMR spectra of PUo and the attribution of different signals are

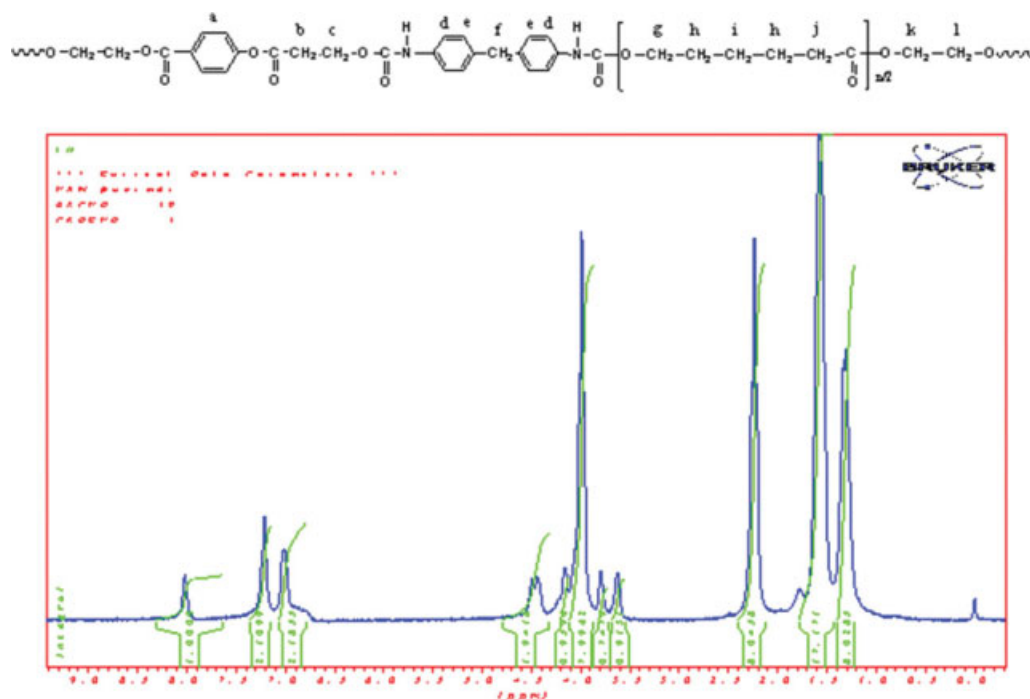


Figure 3 ^1H -NMR (250 MHz, CDCl_3) spectrum of PUo. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

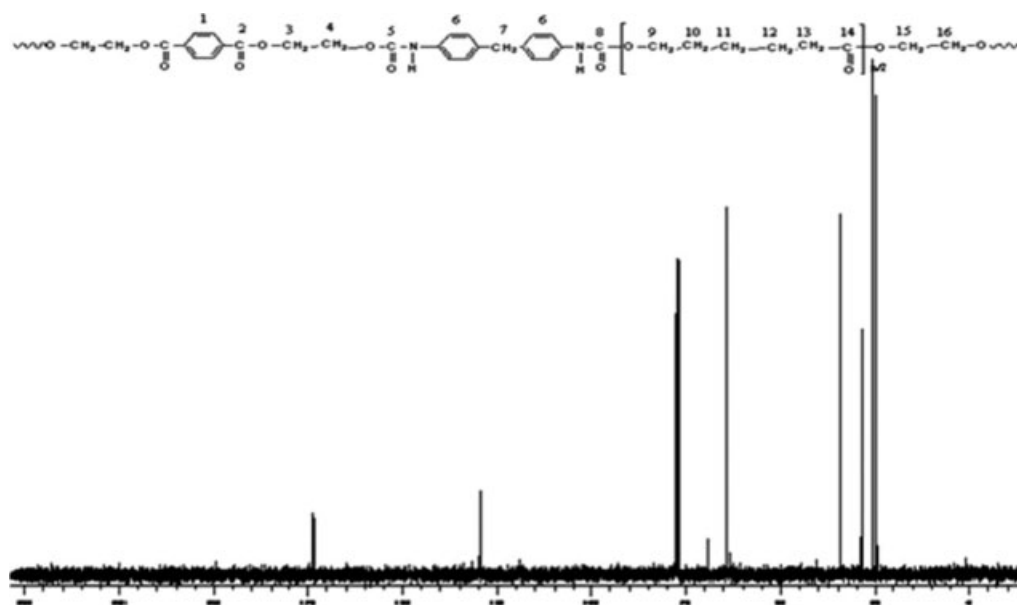


Figure 4 ^{13}C -NMR (CDCl_3) spectrum of PU.

given. All expected signals of protons and carbon atoms are clearly noted. Furthermore, the integration of all proton peaks shows that the structure of PU corresponds to that illustrated in Figures 3 and 4.

From the ^1H -NMR spectrum and according to eq. (1), the TU% composition can be estimated from the integration of BHET aromatic protons at 8.02 ppm, MDI methylene protons at 3.88 ppm and four central protons of PCL at 3.62 ppm. After calculation, the TU% value found for PU is 27%.

$$\text{TU}\% = \frac{I_{8.02}}{I_{8.02} + I_{3.62} + 2I_{3.88}} \times 100 \quad (1)$$

where I is the integration value of signals at these ppm.

This value is consistent with the theoretical value (25%). Moreover, the number average molecular weight determined by SEC, using polystyrene standards, is 34,280 g/mol with a polydispersity index equal to 1.56. This latter result shows that the synthesis in two stages leads to a PU with a relatively narrow molar mass distribution.

One-step synthesis of random polyurethane PU_i

To obtain various structures and properties of PUs, different initial molar mixtures of dihydroxy oligomers (II), BHET (III) and diisocyanate (I) were used. These syntheses are illustrated in Scheme 3 where x and y stand for number of monomer moles.

FTIR, ^1H and ^{13}C -NMR spectra of the obtained PU are identical to those previously recorded for PU₀, the same signals were found at same chemical shifts. From ^1H -NMR spectra, TU% in each PU was calcu-

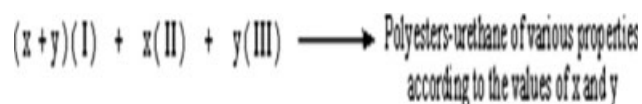
lated according to eq. (1). Table I collects initial molar reagent ratios, composition of PU in TU% determined by ^1H -NMR, number average molar mass M_n , weight average molar mass M_w and polydispersity index (I_w). In addition, we can note that PU₁ synthesized by one-step route has a M_n approximately twice that of PU₀ synthesized by two-step route, in spite of their same molar composition.

The results obtained (Table I) show that all polycondensation reactions were quantitative. For each PU_i, the composition of PUs in TU% is almost equal to the percentage of BHET initially introduced in the reaction mixture. Therefore, we can conclude that all syntheses were effective to insert hard segments according to the desired concentration.

Study of properties

Thermal properties

Figure 5 represents the DSC thermograms of various PUs obtained during the first scan. There is an increase in melting temperature of flexible segments when the composition of PU in TU% rises to 35.80%. Indeed, the melting temperature of PU₁ with 26.50% is 46.7°C, it shifts to 54.1°C in the case of PU₃ with 35.80%. This behavior can be explained by the presence of numerous aromatic rings in the structure of PU, they come not only from BHET molecules but



Scheme 3 Synthesis of PU_i. x and y are number of moles of monomers.

TABLE I
Composition and Average Molar Weight of Different PU

PU	MDI/PCL/ BHET	(TU%) _{the}	% PCL in PU	(TU%) _{exp}	\bar{M}_n (g/mol)	\bar{M}_w (g/mol)	Iw
PUo	2/1/1	25	72.61	27	34,280	53,476	1.56
PU1	2/1/1	25	72.61	26.50	63,298	84,710	1.34
PU2	3/1/2	33.33	61.37	31.50	36,288	64,784	1.76
PU3	4/1/3	37.5	53.12	35.80	14,162	32,498	2.29
PU4	3/2/1	16.66	79.92	15.25	41,949	71,176	1.71
PU5	4/3/1	12.15	82.7	11.70	35,182	59,226	1.68

(TU%)_{the}, theoretical value; (TU%)_{exp}, experimental value.

also from MDI molecules. Besides, PU5 with a lowest TU% composition has a highest melting temperature, we can see that it is the poorest in aromatic rings (Tables I and II). The highest melting temperature for PU5 may be attributed to highest soft segment content. Furthermore, PU5 shows clearly the presence of two melting peaks, due probably to two different crystalline morphologies generated by the influence of two different chemical structures of MDI and BHET. The TU% concentration influences not only the melting temperature, but also the melting enthalpy of soft segments. Indeed, in the case of PU1 and PU3, the soft segment melting enthalpy (ΔH_{ms}) decreases from 24.89 to 21.81 J/g when TU% increases from 26.5 to 35.80%. At the same time, there is an emergence of a melting peak at 189.3°C due to rigid segments of PU3 with the highest TU% value equal to 37.5% (Table II).

Besides, we can observe the appearance of a little exothermic peak located at about 25°C, probably due to the crystallization of flexible segments. The intensity of this peak is relatively slight for PU with a value of TU% superior to 25%, and becomes insignificant for PU4 and PU5 which have the TU% values inferior to this value (Fig. 5, Table II).

By comparing the thermal transitions of PU1 and PUo, both contain the same composition in TU%, they have identical thermal behavior. Thus, thermal properties of PU are not influenced by the method of synthesis.

After a rapid cooling, samples underwent a second rise in temperature. We can see on the thermograms obtained (Fig. 6) that the flexible phase is no longer pure as it was initially, now it contains rigid segments (MDI-BHET) which have not had time to separate more fully because of the rapid cooling applied to the sample. This fact explains the absence of endothermic melting peaks of flexible segments and rigid segments in PUs having TU percentage less than 37%, such as PUo, PU1, PU2, and PU4. The PU5 sample presents a compartment completely different, an important flexible segment exothermic crystallization peak followed by a melting peak in the temperature range from 25 to 50°C. We can note

that this sample contains a lowest value of TU%. The thermogram of PU4 shows a similar feature but both exothermic crystallization and endothermic fusion are hardly seen. PU3 with the highest value of TU% shows a crystallization peak followed by a melting peak of hard segments in the temperature range between 100 and 170°C.

Table II collects the glass transition temperatures of various PU and PCL determined during second scan and the melting temperature of flexible segments determined during first scan. For PU1, PU2, and PU3, T_g and T_m of flexible segments increase with increasing TU%. Some authors^{20,21} explain this phenomenon by strong interaction between flexible and hard segments. The presence of aromatic ring in hard segments could favor the intermolecular interactions with flexible segments and their crystal growth.

Hydrophobic properties

Contact angle measurement gives an idea of material surface polarity. The hydrophobic nature of PUs was

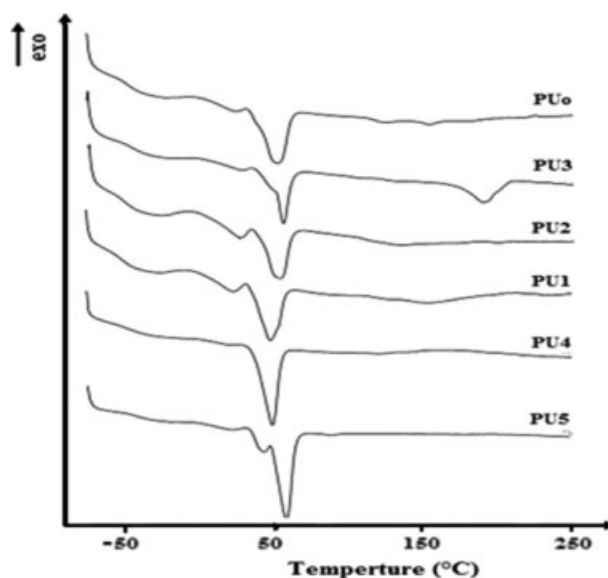


Figure 5 DSC analysis of different PU during the first scan.

TABLE II
Contact Angle, Melting Point, Glass Transition Temperature and Heat of Crystallization (ΔH_c) and Fusion (ΔH_{ms}) During the First and the Second Scan of PU

PU	T_g (°C)	T_m (°C)	ΔH_1 (J/g)		ΔH_2 (J/g)		Contact angle (°)
			ΔH_c	ΔH_{ms}	ΔH_c	ΔH_{ms}	
PCL	-65.7	59.2	0	98.64	0	81.73	–
PUo	-28.3	50.9	0	36.29	0	0	98.1 ± 3.3
PU1	-28.2	46.7	3.59	34.28	0	0	101.2 ± 2.1
PU2	-28	50.9	5.46	37.51	0	0	103.1 ± 40
PU3	-13.4	54.1	0	41.06	0	0	107.2 ± 1.30
PU4	-37.8	47.7	0	39.26	0.84	1.55	99.5 ± 1.5
PU5	-45.1	56.2	0	62.89	51.38	48.54	83.8 ± 3.2

ΔH_1 , heat during the first scan; ΔH_2 , heat during the second scan; ΔH_{ms} , melting heat of soft segments.

determined by their contact angle measured with water. The values of contact angle obtained (Table II) increase with the percentage of BHET in PUs. This result means that the hydrophilic character of films decreases as the percentage of BHET increases. This is mainly due to the hydrophobic character of phenyl rings. Indeed, PU5 with the lowest TU% is the most hydrophilic. Besides, PUo and PU1, both having a same molar composition, but a different monomer unit distribution along polymer chain, do not have the same contact angle value. PU1 ($\theta_i = 98^\circ$) is more hydrophobic than PUo ($\theta_i = 102^\circ$). This result is probably due to the hydrophobic nature of aromatic rings in BHET which are randomly distributed on the polymer chain of PU1 and are easily agglomerated together. Therefore, this structure induces a more important hydrophobicity in PU1 than in PUo, in spite of the fact that their composition in BHET is identical.

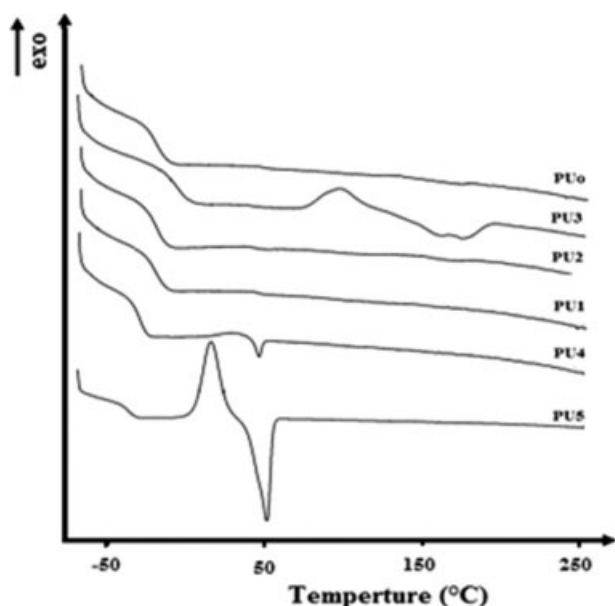


Figure 6 DSC analysis of different PU during the second scan.

Mechanical properties

The stress–strain curves of PU are shown in Figure 7. The numerical values of data are collected in Table III. All curves show the resilience of the sample at break. They have three types of behavior. The first, at low deformation, is attributed to the elastic deformation which characterizes the elastomer phase.²⁷ The second, for plastic deformation between 200 and 400%, characterizes all materials studied and is due to shear-induced crystalline fragmentation. In the last, for deformations higher than 400%, there is an increase in stress which can be attributed to the crystallization of flexible segments. Similar results were found in the case of PCL-based PUs.²⁸

An increase in hard segment content in PUs improves their mechanical properties. Effectively, hard segments can act as a material reinforcing or physical crosslinking in the whole polymer network. Indeed, the Young's modulus increases as TU% increases (Table III), from 10 MPa for PU1 to 20.35 MPa for PU3. The highest Young's modulus is observed for PU5. At this stage of study we can not explain this result which is due perhaps to the presence of high molar concentration of MDI and despite its lowest value of TU%. Probably, both MDI and BHET molecules contribute to this high value of the

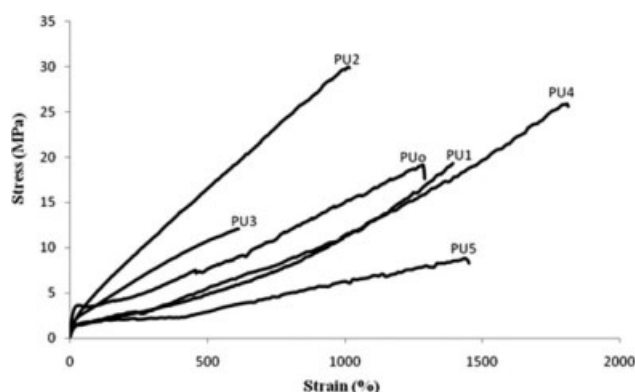


Figure 7 Stress–strain curves of PU films.

TABLE III
Mechanical Properties of PU

	Maximal strength (N)	Deformation at break %	Young's modulus (MPa)	Stress at break (MPa)
PUo	11.58 ± 2.07	1260.89 ± 84.88	37.54 ± 6.12	22.27 ± 1.97
PU1	20.17 ± 5.69	1436.17 ± 84.59	10.03 ± 1.14	26.76 ± 6.08
PU2	17.99 ± 4.53	978.42 ± 65.62	14.26 ± 0.57	28.34 ± 3.88
PU3	15.18 ± 1.90	695.69 ± 135.54	20.35 ± 2.05	11.78 ± 1.81
PU4	16.99 ± 2.11	1752.44 ± 85.84	13.96 ± 1.98	24.26 ± 2.87
PU5	8.46 ± 1.78	1385.26 ± 172.81	30.55 ± 3.37	9.73 ± 2.32

Young's modulus of PU5. Furthermore, the lowest elongation at break of PU3 can be attributed to its low molecular weight.

CONCLUSIONS

The syntheses of PU were implemented in two ways. The first is a two-step synthesis giving a PU with an ordered and regular distribution of three components MDI/PCL/BHET. In the meanwhile, the second synthesis, one-step method, yields a random copolymer. Even with an identical molar composition of monomers, having two different methods of synthesis produces two PUs with different properties, such as molar masses, mechanical properties, etc. The ^1H and ^{13}C -NMR spectra confirm the expected structures of all PU, as well as the FTIR spectroscopy. The thermal and mechanical characterizations highlight the influence of BHET and hard segment content. They enhance the thermomechanical properties of PUs, due to the presence of aromatic rings in their molecules.

The authors are indebted to Philippe Dony for his technical assistance.

References

1. Yeganeh, H.; Jamshidi, H.; Jamshidi, S. *Polym Int* 2007, 56, 41.
2. Hong, J. H.; Jeon, H. J.; Yoo, J. H.; Yu, W. R.; Youk, J. H. *Polym Degrad Stab* 2007, 92, 1186.
3. Borda, J.; Keki, S.; Bodnar, I.; Nemeth, N.; Zsuga, M. *Polym Adv Technol* 2006, 17, 945.
4. Wang, W.; Ping, P.; Chen, X.; Jing, X. *Eur Polym J* 2006, 42, 1240.
5. Reddy, T.; Hadano, M.; Takahara, A. *Macromol Symp* 2006, 242, 241.
6. Lambda, N. M. K.; Woodhouse, K. A.; Cooper, S. L. *Polyurethanes in Biomedical Applications*; CRC Press: New York, 1998; p 205.
7. Lee, S. I.; Yu, S. C.; Lee, Y. S. *Polym Degrad Stab* 2001, 72, 81.
8. Cohn, D.; Stern, T.; Gonzalez, M. F.; Epstein, J. J. *Biomed Mater Res* 2002, 59, 273.
9. Storck, M.; Orend, K. H.; Schmitzrixen, T. *Vasc Surg* 1993, 27, 413.
10. Zhang, L.; Chu, C. C.; Loh, I. H. *J Biomed Mater Res* 1993, 27, 1425.
11. Park, K.; Shalaby, W. S. W.; Park, H. In *Biodegradable gels for Drug Delivery*; Technomic: Lancaster, 1993.
12. Jeong, B.; Bae, Y. H.; Lee, D. S.; Kim, S. W. *Nature* 1997, 388, 860.
13. Cohn, D.; Elchai, Z.; Gershom, B.; Karck, M.; Lazarovich, G.; Sela, J.; Chandra, M.; Marom, G.; Uretzky, G. *J Biomed Mater Res* 1992, 26, 1185.
14. Danielsson, C.; Ruault, S.; Simonet, M.; Neuenschwander, P.; Frey, P. *Biomaterials* 2006, 27, 1410.
15. Peter, S. J.; Miller, M. J.; Yasko, A. W.; Yaszemski, M. J.; Mikos, A. G. *J Biomed Mater Res* 1998, 43, 422.
16. Tatai, L.; Moore, T. G.; Adhikari, R.; Malherbe, F.; Jayasekara, R.; Griffiths, I.; Gunatillake, P. A. *Biomaterials* 2007, 28, 5407.
17. Yen, M. S.; Tsai, H. C.; Hong, P. D. *J Appl Polym Sci* 2007, 105, 1391.
18. Mondal, S.; Hu, J. L. *Polym Int* 2006, 55, 1013.
19. Sarkar, D.; Yang, J. C.; Lopina, S. T. *J Appl Polym Sci* 2008, 108, 2345.
20. Vlad, S.; Oprea, S. *e-Polymers* 2008, 27, 1.
21. Li, F.; Hou, J.; Zhu, W.; Zhanc, X.; Xu, M.; Luo, X.; Ma, D.; Kim, B. *J Appl Polym Sci* 1996, 62, 631.
22. Lowry, K. J.; Hamson, K. R.; Bear, L.; Peng, Y. B.; Celaluce, R.; Evans, M. L.; Anglen, O. J.; Allen, W. C. *J Biomed Mater Res* 1997, 36, 536.
23. Shaik, A.; Richter, M.; Kricheldorf, H. R.; Krüger, R. P. *Polym Chem* 2001, 39, 3371.
24. Witt, U.; Muller, R. J.; Deckwer, W. D. *J Environ Polym Degrad* 1997, 5, 81.
25. Lee, S. H.; Lim, S. W.; Lee, K. H. *Polym Int* 1999, 48, 861.
26. Lim, K. Y.; Kim, B. C.; Yoon, K. J. *J Polym Sci Part B: Polym Phys* 2002, 40, 2552.
27. West, J. C.; Cooper, S. L. In *Thermoplastic Elastomers, in Science and Technology of Rubber*; Eirich, F. R., Ed.; Academic Press: New York, 1978; p 531.
28. Heijkants, R. G. J. C.; Van Calck, R. V.; Van Tienen, T. G.; de Groot, J. H.; Buma, P.; Pennings, A. J.; Veth, R. P. H.; Schoute, A. J. *Biomaterials* 2005, 26, 4219.