

Segmented Poly(urethane-urea) Elastomers Based on Polycaprolactone: Structure and Properties

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ABSTRACT: A series of segmented poly(urethane-urea) polymers have been synthesized varying the hard segments content, based on the combination of polycaprolactone diol and aliphatic diisocyanate (Bis(4-isocyanatocyclohexyl) methane), using diamine (1,4-Butylenediamine) as the chain extender. The microstructure and properties of the material highly depend on the hard segments content (from 14 to 40%). These PUUs with hard segment content above 23% have elastomeric behaviors that allow high recoverable

deformation. The chemical structure and hydrogen bonding interactions were studied using FTIR and atomic force microscopy, which revealed phase separation that was also confirmed by DSC, dynamic-mechanical, and dielectric spectroscopy. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2093–2104, 2011

Key words: poly(urethane-urea); block copolymers; elastomers; phase separation; polycaprolactone

INTRODUCTION

Segmented Polyurethane (PU) and Poly(urethane urea) (PUU) have received much attention for the development of biodegradable polymers because of their great potential in the tailoring polymeric structure, and their role in obtaining mechanical properties and biodegradation rates to cover a variety of medical applications.^{1,2} PU and PUU can be found in vascular applications, such as pacemaker insulation, heart valves, and intra-aortic balloons. Pellethane (Dow Chemical), Biomer (Ethicon) and Tecothane (Thermedics) are examples of commercially available PU/PUU. They are nondegradable materials containing a polyether soft segment and a hard segment derived from an aromatic diisocyanate. PU/PUU have shown promising results in applications, such as ligament reconstruction,^{3,4} meniscus replacement,^{5,6} and bone regeneration.⁷ For example, the biodegradable PU Artelon (Artimplant, Västra Frölunda, Sweden), known for its long and controlled *in vivo* degradation time, has been used in several medical applications. *In vitro* and *in vivo* studies have demonstrated its safety and excellent biocompatibility.⁴

PUUs are blends of copolymers that present alternating hard and soft segment sequences. Hard segments are blocks formed by the reaction of a diisocyanate with a low molecular weight diamine, whereas the soft segments are blocks of a high molecular weight diol. Immiscibility between soft and hard segments induces microphase separation or segregation, which is a factor that highly influences the biocompatibility of this multiblock copolymer.² By adding diamine chain extenders rather than diols, urea groups are included at the hard segment, resulting in the formation of multiple hydrogen bonds between proton donors (urethane N—H and urea N—H groups) and proton acceptors (urethane C=O, urea C—O and C—O—C groups) in the hard domain.⁸ These hard segment domains play an important role in the mechanical behavior of the material, acting as physical crosslinks and/or as fillers of the rubbery soft segment matrix that increase the elastic modulus of the rubber, such results are higher than typical chemically crosslinked elastomers. Another interesting characteristic of PU/PUU thermoplastic elastomers is the possibility of being processed by conventional molding techniques.

Polycaprolactone (PCL) is commonly used as soft segment in the synthesis of biodegradable polyurethanes.⁹ PCL is a semicrystalline polymer that degrades slower than both polylactide and polyglycolide and thus, it is preferably used for several long term applications.¹⁰ It is degraded *in vivo* through hydrolysis and enzymatically, and a part of the

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degradation occurs by intracellular mechanisms.¹¹ Recent works have verified the cytocompatibility and noncytotoxicity of PCL based PUU elastomers.^{12–14}

On the other hand, methyl diisocyanate (MDI), has been used for the synthesis of medical-grade polyurethanes, despite the observation that their degradation products are suspected to be carcinogens, namely methylene diamine (MDA).¹⁵ Nevertheless, a solution to the potential carcinogenic effect of MDA has already been proposed that is the use of a hydrogenated version of MDI, bis(4-isocyanatocyclohexyl)methane (HMDI). Aliphatic diisocyanates, such as lysine-methyl-ester diisocyanate or 1,4-butanediisocyanate are also used to reduce the toxicity of the degradation products. An advantage to the use of these is the ease of crystallization of the isocyanate groups, which is a variable that allows modifying the mechanical properties of the final polymer and increasing the microphase separation.¹⁶

The majority of the PUUs produced commercially are based on polyesters, mainly because of their mechanical properties (tensile and tear strength and abrasion resistance). However, they are susceptible to hydrolytic degradation when implanted in the body, even for short periods of time.^{2,17,18} Thus, when looking for more biostable materials, polyols based on ether links have been used, although they are still susceptible to degradation by scission of the urethane and CH₂-O links.¹⁹ The combination of ether and ester groups, include both hydrophilic and hydrophobic characteristics, respectively.^{20,21} If a diamine such as Putrescine,^{22–26} which is a growth factor essential for the cell division in mammals²⁶ is added at the backbone of the PUUs, during the chain extension step, the mechanical properties can be improved as a result of a higher molecular weight. These, then allow to obtain a variety of phase-separated morphologies.²⁷

In this work, we analyze the structure of segmented PUU synthesized from an aliphatic diisocyanate, HMDI, polycaprolactone-diol of high molecular weight, and 1-4 diaminobutane (putrescine) as the chain extender. It is expected that this system to be biodegradable with noncytotoxic degradation products, in according to the pointed out in the preceding paragraphs. The obtained materials are similar in structure to those synthesized by Guan et al.^{13,14} except by the isocyanate (HMDI). The effect of increased hard segments content on the thermal, mechanical, and dielectric properties is analyzed.

EXPERIMENTAL

Materials

HMDI, Stannous octoate (SO), and Dimethylformamide anhidro (DMF) were purchased from Aldrich

and 1-4 diaminobutane and Isopropyl alcohol (IPA) were purchased from Fluka and used as received.

Polycaprolactone-diol (Mn 2000, purchased from Aldrich) was dried under vacuum at 55°C for 24 h to remove moisture. This polymer contains an ethylene glycol unit in the center of each polymer chain since its polymerization is initiated by diethylene glycol.

Synthesis of PUUs

In this work, the hard segment fraction (wt % HS) was calculated from the weight ratio of diisocyanate and butanediamine to that of all the reactants, including diisocyanate, butanediamine, and polyol. In other words, the content of hard segments was based on the content of urea-urethane groups,²⁷ as shown in eq. (1):

$$\text{wt \% HS} = \frac{100(R)(M_{\text{di}}) + (R - 1)(M_{\text{da}})}{M_{\text{PCL}} + R(M_{\text{di}}) + (R - 1)(M_{\text{da}})}, \quad (1)$$

where the variable M refers to the molecular weight of the monomer, R is the mole ratio of isocyanate to diol (NCO/OH), and the subindexes PCL, di and da refer to polycaprolactone-diol, diisocyanate, and diamine, respectively. In the case of polycaprolactone-diol the average molecular weight was included in eq. (1).

To obtain the linear polymer (Fig. 1), a molar ratio NCO:OH and NH₂ was maintained at 1 : 1. PUUs were synthesized by two-step polymerization (pre-polymer method) under an inert atmosphere of high purity nitrogen, in a 250 mL three-neck round-bottomed flask equipped with a stirrer and a thermometer. A 10% w/v solution of PCL in DMF was mixed with the catalyst, stannous octoate (about 0.01 wt %) at 40°C for 30 min to obtain a homogenous solution. In a first step an excess of diisocyanate was added to obtain an isocyanate-terminated prepolymer at several NCO/OH ratio (1.2, 2, 3, and 4), and the reaction was left for 3 h at 75°C. The prepolymer solution was cooled to room temperature and chain extension step was performed adding slowly stoichiometric amounts of putrescine under vigorous magnetic stirring for 180 min. The reaction was completed by increasing the temperature to 75°C for 180 min.

The solution was cooled (25°C) and the polymer was precipitated in cool distilled water and washed in IPA at room temperature for 3 days, changing the IPA every 12 h, to remove unreacted monomer. The samples were then dried at 50°C for 24 h under reduced pressure. A series of four PUUs with hard segment contents ranging between 14 and 40% were synthesized. The sample designation is included in Table I.

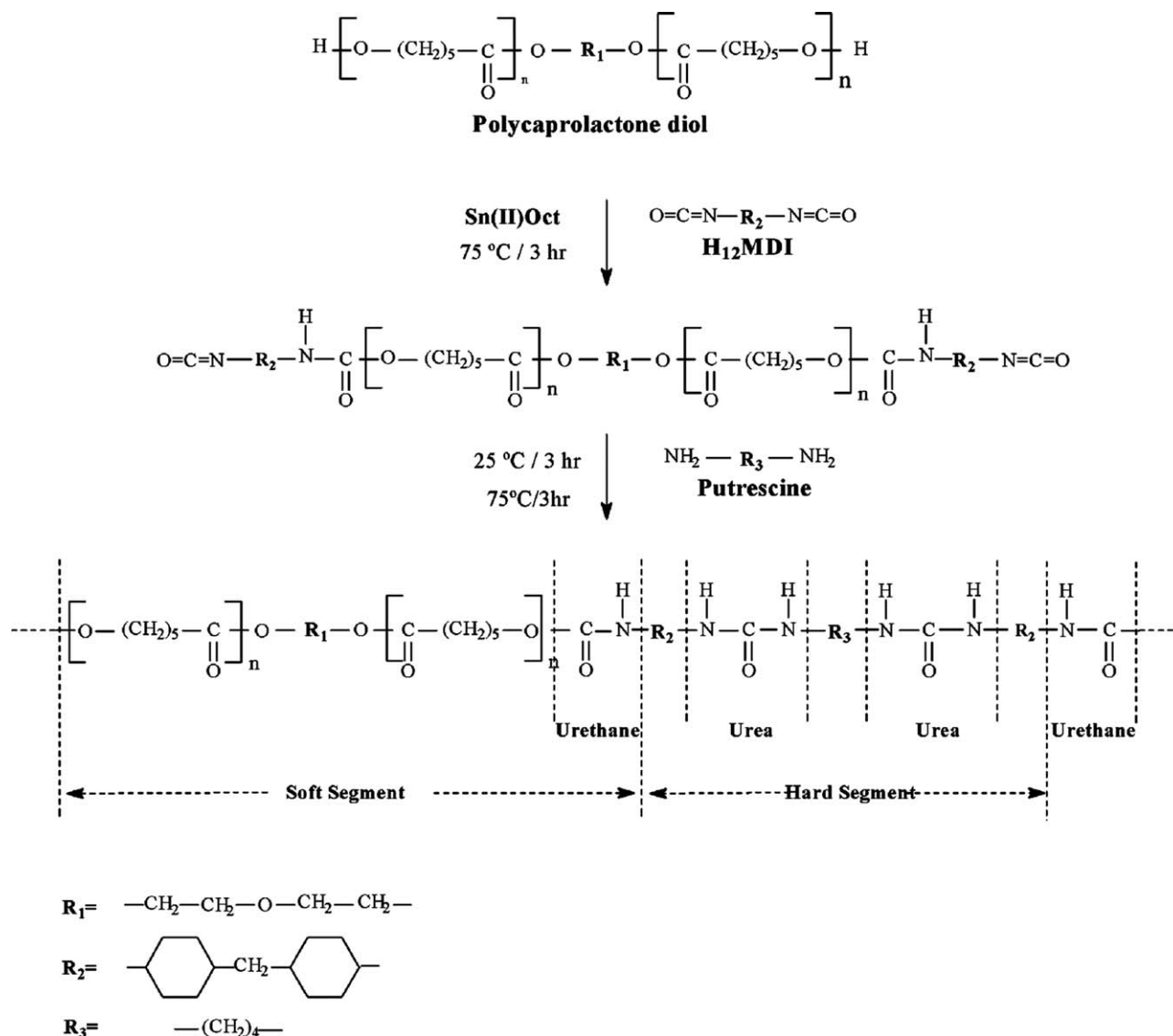


Figure 1 ATR-FTIR spectrum of PUUs samples, Polyurea and PCL as references.

Synthesis of polyurea

The polymerization of polyurea was carried out at room temperature under stirring. A solution of HMDI in DMF (10% w/v) was placed in a three-neck reactor, and putrescine was added (equimolar ratio 1 : 1 of NCO : NH₂) dropwise under vigorous stirring. The reaction took place immediately and a white precipitate was formed.

After 30 min, the polymer was removed, washed repeatedly with an ethanol/water mixture (75 : 25, v/v), and dried under vacuum for 24 h at 50°C.

Film preparation

PUUs were dissolved (10% w/v) in DMF at 90°C for 2 h and subsequently poured onto Teflon plates. The solvent was allowed to evaporate at room temperature for 24 h, and later the samples were dried at

50°C for 48 h under low pressure. The resulting films were ~ 400 μm thick. The urea films subjected to infrared characterization were obtained by compression molding.

Measurements

Gel permeation chromatography (GPC) was used to determine the average molecular weights and polydispersity of the synthesized. A HP/Agilent 1100 GPC (CA) instrument equipped with a refractive index detector (RID A) was used. The mobile phase was THF at a flow rate of 1 mL/min. Calibration was performed with polystyrene standards. The polymers were dissolved (1.5% w/v) in THF by stirring at 65°C for 60 h and 20 μL was injected.

Phase images were obtained using an atomic force microscope (AFM) Nanoscope IIIa system from Digital Instruments (Santa Barbara, CA). Experiments

TABLE I
Composition and Some Characteristic Parameters of the Thermal Properties of the PUUs Samples

Samples	Molar composition HMDI/PCL/ BDA	Hard segments contents ^a	Molecular weight (Mw)	T_g^b (°C)	T_m^b (°C)	$T_{\alpha\text{DMA}}^c$ (°C)	ΔC_p (J/g°C) (1st/2nd heating DSC scan)	Characteristics
PCL2000	–	–	2×10^3	–64	46–51	–	0.22/0.26	Brittle, opaque
PUU14	1.2/1/0.2	14.2 \approx 14%	2.5×10^4	–48	46.47	–31	0.30/0.38	Brittle, opaque
PUU23	2/1/1	23.5 \approx 23%	2.6×10^4	–53	–	–38	0.55/0.62	Lightly Flexible, translucent
PUU32	3/1/2	32.5 \approx 32%	2.8×10^4	–57	–	–40	0.43/0.50	Slightly elastic, clear
PUU40	4.5/1/3.5	39.6 \approx 40%	–	–57	–	–44	0.38/0.44	Tough, rubbery, opaque

^a Obtained from eq. (1).

^b Obtain by DSC (first heating).

^c Temperature of the maximum of the loss tangent in the main relaxation process measured by DMA (see text).

were performed in tapping mode under ambient conditions. Images were acquired with a 2.8 N/m force constant tip. The tapping frequency was around 10% lower than the resonance frequency (75 KHz). The ratio between the setpoint and drive amplitude was set to 0.8.

Thermal properties were determined by differential scanning calorimetry (DSC) from a Mettler Toledo DSC-823e system (Zürich, Switzerland), between -100 and 140°C , the heating and cooling rate of the scans was $10^\circ\text{C}/\text{min}$. Nitrogen was used as the purge gas.

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra of PUUs were recorded with a Nicolet Protegé 460 (Wisconsin) between 600 and 4000 cm^{-1} with a resolution of 8 cm^{-1} , using film samples cast from 10 wt % solutions in DMF and dried for 24 h in a vacuum oven at 30°C .

Dynamic mechanical analysis (DMA) was performed using a Perkin-Elmer DMA-7 (Norwalk, CT) at a frequency of 1 Hz. The temperature dependence of the storage modulus and loss tangent were measured in the temperature range between -100 and 100°C at a heating rate of $5^\circ\text{C}/\text{min}$. Samples were cut from the dried films with approximate dimensions $12 \times 3 \times 0.4\text{ mm}^3$.

Uniaxial stress-strain experiments were performed with a Shimadzu AG-100 KN equipment (Kyoto, Japan) at 25°C at a cross-head speed of $125\text{ mm}^\circ\text{min}^{-1}$. Samples were cut from a sheet of PUUs film of about 0.4 mm thickness. The specimen gauge length was about 45 mm long and 7 mm wide.

Thermogravimetric analysis (TGA) was carried out on PUUs samples using a Perkin-Elmer TGA-7 analyzer (Norwalk, CT). Approximately 8 mg of each sample was heated from 50 to 600°C in a nitrogen atmosphere at the rate of $10^\circ\text{C}/\text{min}$.

Dielectric relaxation spectroscopy (DRS) experiments were performed using an impedance analyzer Alpha-S (Hundsangen, Germany). The temperature control was assured by the Quatro cryosystem from Novocontrol GmbH. The real and imaginary parts of

the complex dielectric permittivity were measured isothermally from 10^{-1} to 10^6 Hz. The samples were kept between gold-plated stainless steel electrodes and the temperature was varied from -140 to 80°C at intervals of 5°C .

RESULTS

A series of four poly(urethane-urea) polymers were synthesized (Table I). The polyurethanes obtained in the study were linear materials and soluble in polar solvents, such as dioxane, THF, DMF, and DMSO. These solvents were chosen for freeze drying tests whose results will be published in a later article. The samples containing 14 and 23 wt % of hard segments were soluble in dioxane, THF, and DMF at 120°C for 48 h. On the other hand, all samples were soluble in DMSO at temperatures close at 90°C for 48 h, which is more polar than the other solvents. The solubility of the samples was not tested with apolar solvents. The molecular weights of PUUs were less than 3×10^4 Da. A polyurea sample was also synthesized as a reference for the interpretation of the properties of the PUUs. The polyurea was dissolved in organic solvents such as acetic acid, at 50°C for 24 h.

FTIR analysis

Figure 2 shows the FTIR spectra, which are similar in PUUs containing different contents of hard segments. Spectra were similar to those obtained by Guan et al.¹⁴ It is worth noting the absence of the 2260 cm^{-1} band that is characteristic of the unreacted isocyanate groups. Stretching vibrations of the ester groups are assigned to the 1060 , 1160 , and 1239 cm^{-1} bands. The peak at 1536 cm^{-1} is characteristic of the carbonyl stretching vibration, which is very intense and clearly increase with the content of hard segments. But also the amide II peak (a combination peak of N–H bending and C–N stretching vibration) at 1560 cm^{-1} is studied. The urea carbonyl

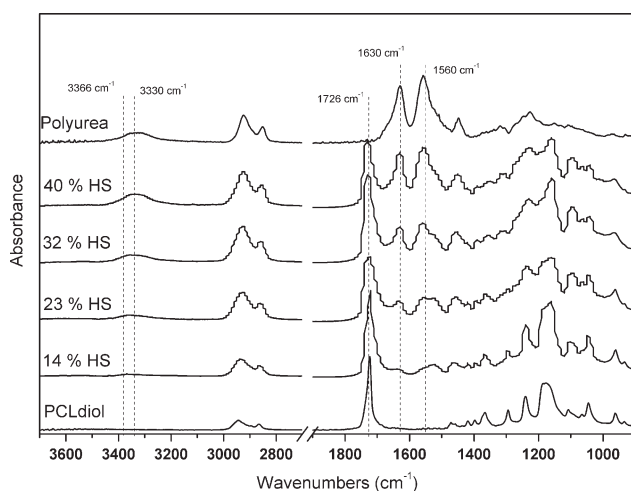


Figure 2 Synthesis of segmented poly(urethane-urea).

(hydrogen bonded) peak at around $1640\text{--}1629\text{ cm}^{-1}$, which also increases with the content of hard segments indicating the presence of orderly arrangement of urea groups.²⁸ The characteristic bands of ester and urethane free carbonyls appear overlapped between $1735\text{ and }1710\text{ cm}^{-1}$. The absorption peaks at $2854\text{ and }2924\text{ cm}^{-1}$ correspond to symmetric and asymmetric CH_2 groups, respectively. Bands at $1458, 1420, 1394, \text{ and }1365\text{ cm}^{-1}$ correspond to various modes of CH_2 vibration.

The absorbance at 1100 cm^{-1} was attributed to the ether group at the center of the polycaprolactone segment. The absorption band at 3330 cm^{-1} is caused by hydrogen-bonded N-H (urea and urethane) stretching, which increase with the content of hard segments. The absorption band in PUUs with lower contents of HS appears at 3366 cm^{-1} and is associated to nonbonded free N-H (Fig. 3).

The peak intensities of the hydrogen-bonded urethane carbonyl groups depend on the increase in hard segments content and it is correlated with the decrease

observed in the peak intensity of the free carbonyl band (nonbonded).

DSC analysis

The calorimetric results of PUU samples [Fig. 4(a)] show the effect of the hard segment content onto the crystallization and glass transition behavior of the soft segments. An endotherm at 120°C was attributed at the hard segments. The first heating scan of the sample containing 14% hard segments has a melting endotherm associated with the polycaprolactone segments. The melting peak appears at a temperature slightly higher than in the polycaprolactone-diol used in the synthesis process whose thermogram is also shown in Figure 4(a) for comparison. Note that in the heating scan of PCL a double peak appears due to the superposition of the exothermal crystallization that take place during the heating scan, immediately after the first endotherm. In the PUU containing 23 or 32% HS a small endotherm appears in the same temperature interval as well, showing that some PCL crystallization is also possible in these samples. On the contrary, the PUU40 sample shows a broad endotherm similar to the heating thermogram of pure polyurea also included in Figure 4(a).

On the other hand the thermograms show the glass transition of PCL blocks in the same temperature region than in the PCL-diol but slightly shifted towards higher temperatures (Table I).

These heating scans are recorded with the samples as were obtained from the synthesis process in which the last stage consisted in solvent casting at 50°C . Later a cooling scan at $10^\circ\text{C}/\text{min}$ showed that only the sample containing 14% HS was able to crystallize, showing an exotherm shift around 10°C towards lower temperatures with respect to pure PCL-diol [Fig. 4(b)]. The rest of samples just show

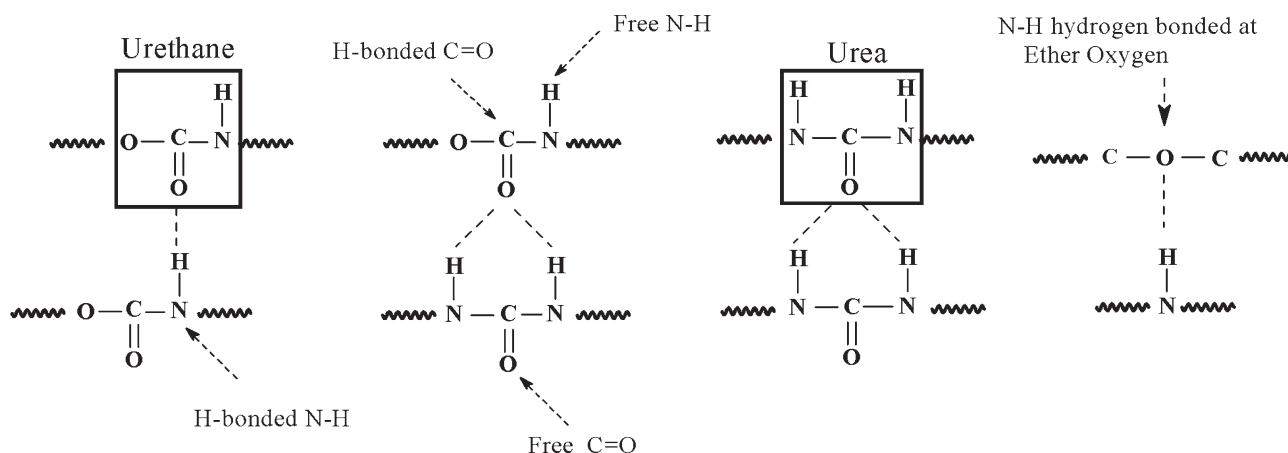


Figure 3 Possible intermolecular interchain interactions in segmented poly(urethane-urea) elastomers.

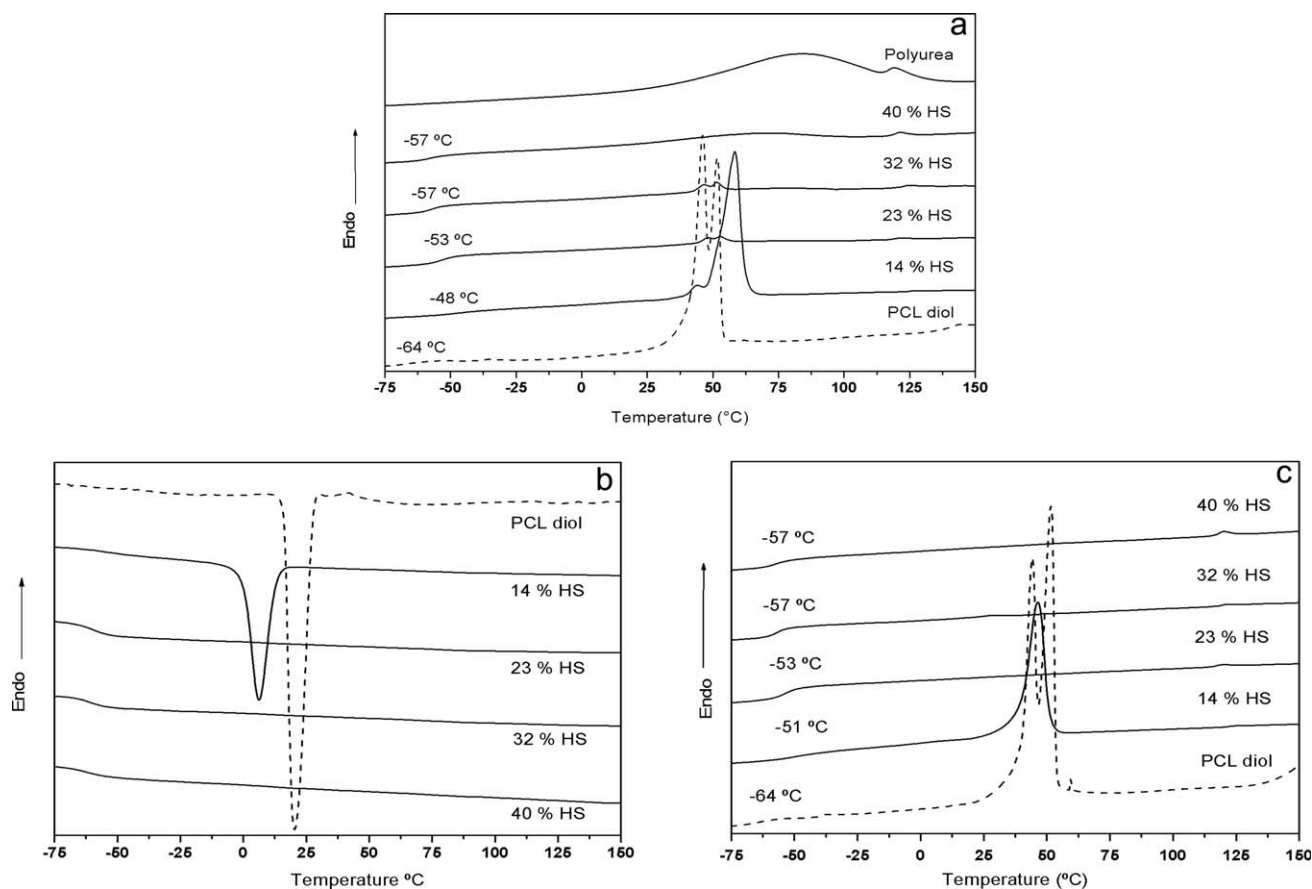


Figure 4 DSC thermograms of PUUs samples: (a) first heating at 10°C/min, (b) first cooling at 10°C/min, (c) second heating at 10°C/min.

the glass transition in the temperature range around -60°C . The second heating scan shows only the glass transition of PCL blocks in all samples with the exception of those containing 14% HS, which melt at a temperature close to that of the PCL-diol [Fig. 4(c)]. The enthalpy of melting for sample PUU14 is around 40% smaller than the pure PCL sample. The heat capacity increment and the glass transition temperature are always higher in the second scan than in the first (Table I).

AFM analysis

AFM images of PUU samples (Fig. 5) show the presence of a phase separation with phase domains in the nanometer scale. The phase morphology strongly depends on the sample composition. The structure observed in the phase image in the case of the PUU14 sample [Fig. 5(b)] consists of large aggregates aligned parallel to each other. This structure was found only in the surface of sample PUU14, and is related to PCL crystallization, disappearing in sample PUU23 in which a homogeneous distribution of small domains appears [Fig. 5(d)]. These domains grow in the sample PUU32, which shows a

great dispersion of domain size, with most of the aggregates ranging between 20 and 50 nm in size. Some of them even reach 100 nm. The sample with the highest hard segment content shows a very uniform distribution of domains that seem to percolate [Fig. 5(h)]. The comparison of phase and height images allows for ascribing the structure shown by phase measurements to differences in the viscoelastic properties of the soft and hard domains (or crystalline and amorphous domains in the case of sample PUU14) and not to artifacts produced by the surface topography.

DMA analysis

In the temperature interval of our dynamic-mechanical experiments the polycaprolactone shows only the main relaxation, associated with the co-operative rearrangements of the polymer chains in the amorphous phase. A secondary relaxation appearing at much lower temperatures, which will be detected in dielectric experiments.^{29,30} The dynamic mechanical results of PUU samples (Fig. 6) present this relaxation process in the temperature interval between -70 and -10°C . The temperatures of the maximum

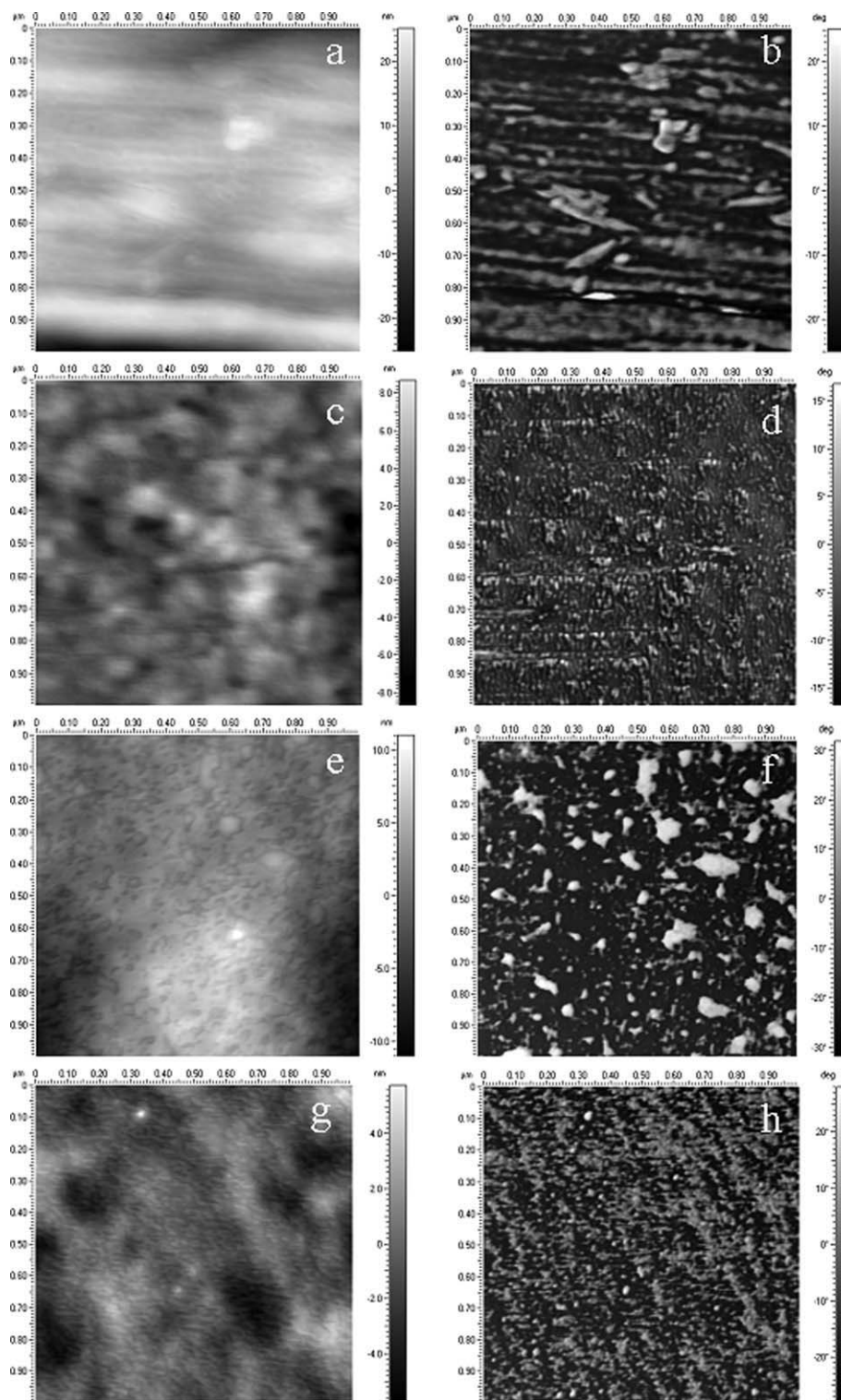


Figure 5 AFM height (left) and phase (right) images of $1 \mu\text{m}^2$ of the PUUs films surface: (a, b) 14% HS, (c, d) 23% HS, (e, f) 32% HS and (g, h) 40% HS.

of the loss tangent peak, which we will call $T_{\alpha\text{DMA}}$ have been listed in Table I. This temperature is generally situated around 15° above the calorimetric glass transition temperature, T_g . It is higher in the sample containing 14% HS than in the rest of the samples. The drop of the elastic modulus in the

relaxation process highly depends on the HS content of the polymer [Fig. 6(a)]. At temperatures above the transition in the region of the elastomeric plateau, the highest modulus corresponds to the PUU14 sample while that of PUU23 is the lowest one increasing from this HS content on, a feature

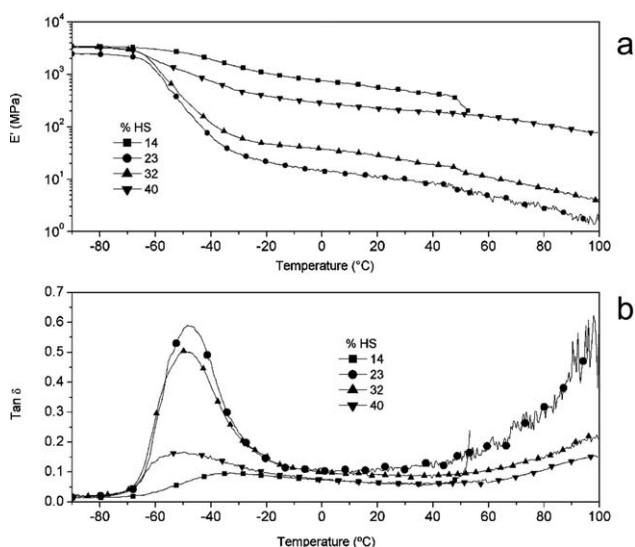


Figure 6 DMA curves of PUUs: (a) storage modulus, (b) $\tan \delta$.

that as we will discuss below must be related to the crystallinity and crosslinking density of the polymer.

TGA analysis

The TGA curves of PUUs show a two-step decomposition, which are related at the existence of two different segments in the structure: hard and soft segments. The degree of phase separation plays a role in the decomposition of the polyurethanes as it is observed in the Figure 7. Apparently, a low content of HS improve the phase separation allowing at both soft and hard segments to crystallize to delay the degradation rate; higher content of HS induce a poor phase separation (phases mixed) that increase the degradation rate of the urea and urethane

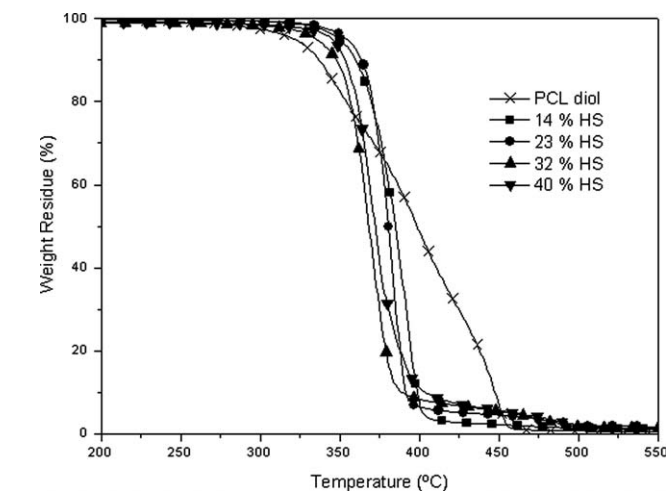
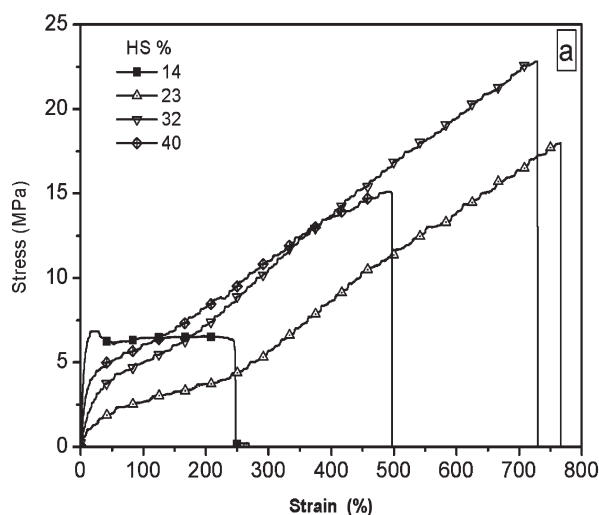


Figure 7 TGA thermograms of synthesized PUUs.

groups; however, mixture of phases allowed to improve the thermal stability of the soft segments (secondary step) even after the dissociation of hydrogen bonds interurethane.

Stress–strain measurements

Results of the elastic modulus and ultimate stress obtained by tensile testing in PUU samples at room temperature are shown in Figure 8. The sample with 14% HS shows a behavior characteristic of ductile materials. This sample presents the highest elastic modulus, and the lower tensile strength and elongation at break. PUUs with the highest hard segment contents show a different stress–strain curve with a behavior typical of the elastomeric materials. The modulus of PUU23 decreases one order of magnitude with respect to PUU14 and then increases with

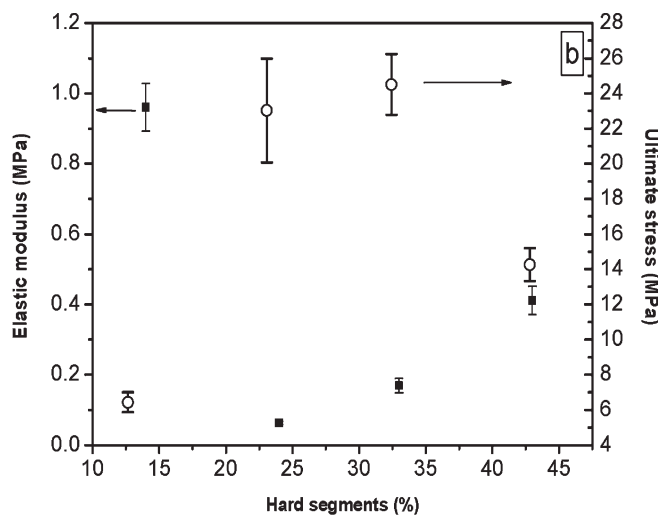


Figure 8 Results of the stress–strain measurements showing the effect of increase the hard segments content: (a) typical stress–strain curves of PUUs samples, (b) Dependence of the elastic modulus (■) and ultimate stress (○) on hard segment contents of the samples.

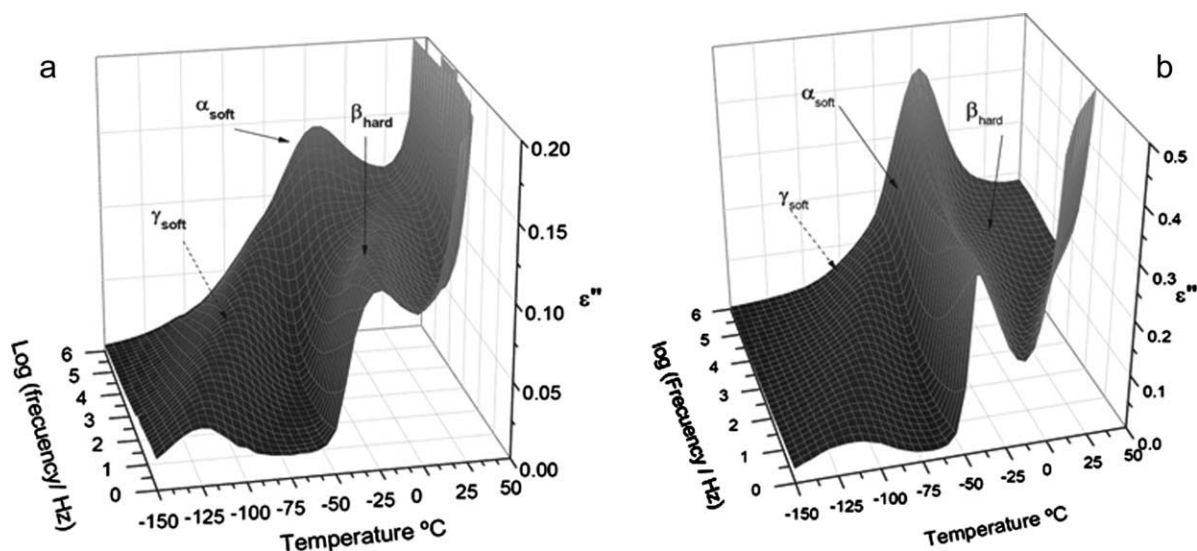


Figure 9 Three-dimensional plots show the shift of the three relaxation processes with frequency and temperature for PUU14 (a) and PUU40 (b) (note the change of scale in the later with respect to figures 6a).

increasing HS content, in good agreement with the values of the storage modulus measured by DMA in the elastomeric plateau region. The mechanical properties obtained in this work were similar to the observed by Guan et al.^{13,14}

On the other hand the ultimate stress and the elongation at break in PUU23 and PUU32 are also one order of magnitude higher than in PUU14 and decrease in PUU40, which is stiffer material due to the high HS content.

Dielectric relaxation spectroscopy analysis

The dielectric relaxation spectrum of PCL-diol shows two relaxation processes, a secondary relaxation that will be called hereafter γ_{DRS} and the main dielectric relaxation associated with cooperative conformational rearrangements of the polymer chains in the amorphous phase, which will be called α_{DRS} (Fig. 9). These relaxation processes were already described in previous papers^{30–32} both in PCL-diol and in high molecular weight PCL. In the PUU samples, γ_{DRS} and α_{DRS} also appear and should be related to the soft PCL-diol segment. In addition, a third relaxation, β_{DRS} , with the characteristics of a secondary relaxation is shown clearly in the plots of Figures 9(a,b). This relaxation is ascribed to the local motions of the permanent dipoles of the urethane and urea groups in the hard segment.

The β_{DRS} can hardly be characterized, due to the overlapping with α_{DRS} since the intensity of the latter is higher. The position of the local γ_{DRS} relaxation in the temperature axis does not systematically depend on the hard segment content.

At low frequencies, β_{DRS} relaxation appears at temperatures below the temperature interval of the α_{DRS} relaxation. Thus the dependence of the latter on the fraction of hard segments in PUUs can be clearly observed [Fig. 10(a)]. At higher frequency, as shown in Figure 10(b), β_{DRS} relaxation appears at temperatures immediately higher than α_{DRS} and both relaxations partially overlap. The strength of the main dielectric relaxation of the PCL segments in PUU14 is in the order of that of pure PCL-diol but shifts towards higher temperatures around 15°, as shown in Figure 10(a) at 1 Hz. The broad relaxation at 10 kHz in this sample is the result of the superposition of β_{DRS} and α_{DRS} , which have similar intensities in this sample. The behavior of sample PUU23 is completely different the α_{DRS} is much higher than in PUU14 or PCL-diol. For samples PUU32 and PUU40, the height of the “ ϵ ” peak decreases with the hard segment content of the PUU.

The temperature dependence of the relaxation times τ_{max} obtained from the maxima of “ ϵ ” is shown in an Arrhenius diagram [Fig. (11)]. The maximum of frequency ($\tau_{max} = 1/2\pi f_{max}$) related with the secondary relaxation processes has been calculated from isothermal curves. From these plots an apparent activation energy $E_a = 99 \pm 1 \text{ kJ mol}^{-1}$ can be calculated for the β_{DRS} relaxation of PUU23, PUU32, and PUU40, while for PUU14 a slightly higher value was found ($E_a = 105 \pm 1 \text{ kJ mol}^{-1}$). In the case of γ_{DRS} relaxation a small displacement towards a higher temperature is shown compared to the PCL diol. For PUU14 and PUU40, $E_a = 41 \pm 1 \text{ kJ mol}^{-1}$ and for PUU23 and PUU32 a value $43 \pm 1 \text{ kJ mol}^{-1}$ was obtained. These results show a slight increase

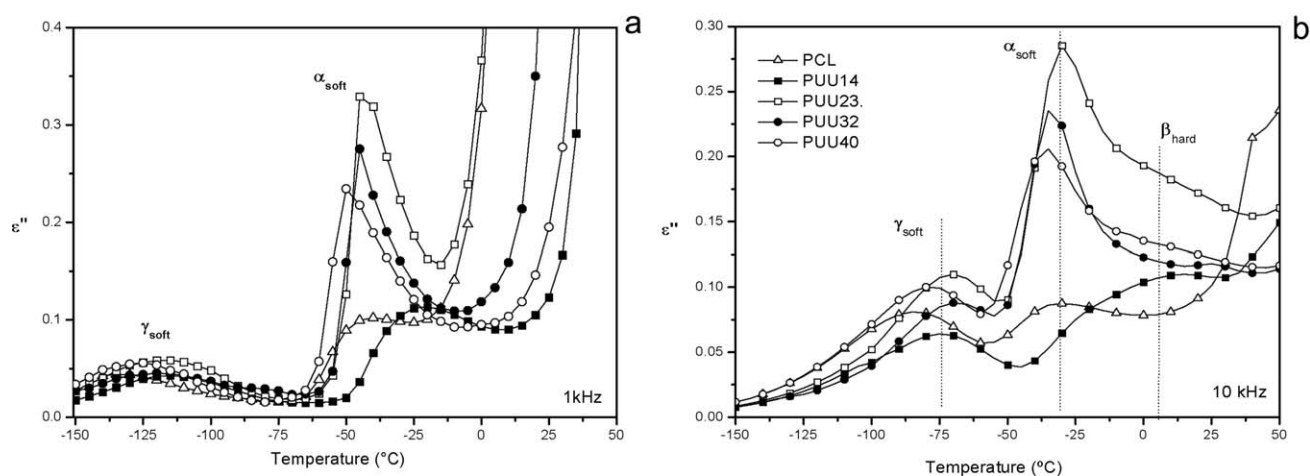


Figure 10 Temperature dependence of the dielectric loss, ϵ'' at 1 Hz (a) and 10 kHz (b) for PCL diol (Δ), PUU14 (\blacksquare), PUU23 (\square), PUU32 (\bullet), and PUU40 (\circ).

with respect to the E_a obtained for the PCL diol ($37 \pm 1 \text{ kJ mol}^{-1}$).

In the inset of Figure 11, the frequency position of the maxima values of " ϵ'' " corresponding to α_{DRS} relaxation, obtained from isochronal curves, is shown. In the case of the PCL diol and PUU14, α_{DRS} shows the characteristic curvature of the co-operative main relaxation process, while in the other samples, the Arrhenius diagram is more linear. The main process α_{DRS} in sample PUU14 is shifted to higher temperature respect to PCL diol. Nevertheless in the remaining samples this process shows a displacement to lower temperatures.

DISCUSSION

A series of block copolymers were synthesized in this work, one of which is polycaprolactone while the other is the urea hard segment. These structures allow the modification of the mechanical behavior of PCL, modulating its mechanical properties between those corresponding to a stiff semicrystalline polymer and those of an elastomer with up to 75% deformation at break. Interestingly enough, solubility with some specific solvents seems to indicate that no chemical crosslinks appear due to the synthesis conditions. Nevertheless hydrogen bonding proved by FTIR spectroscopy seems to be enough to ensure the recovering of deformation.

The DSC results show that the ability of PCL to crystallize is maintained in PUUs up to a certain content of hard segments. The cooling scan shows that the kinetics of crystallization on cooling is modified by the presence of the hard segments and the melting enthalpy shows that a significantly smaller fraction of PCL chains participate in the crystalline phase. This means that the presence of the hard segments in this sample is a significant constraint for

PCL segment diffusion during crystal growth although it does not impede crystallization. On the other hand, the temperature of the melting peak in PUU14 crystallized from the melt is $\sim 47^\circ\text{C}$, while in high molecular weight PCL a value around 60°C is obtained. This difference gives information about the smaller crystal size of PCL segments in PUU. PUUs with higher content of hard segments show no trace of crystallization in the cooling or heating scans (Fig. 4). PCL segments in polymer networks of block copolymers of PCL (with molecular weight 2000 Da) and hydroxyethyl acrylate were able to crystallize when the HEA content was below 30% by weight.³² Van Bogart et al.³³ observed a similar behavior in HMDI-BDO-PCL samples with relatively low hard segment content; at higher hard segment content the crystallization of the soft segments is suppressed.

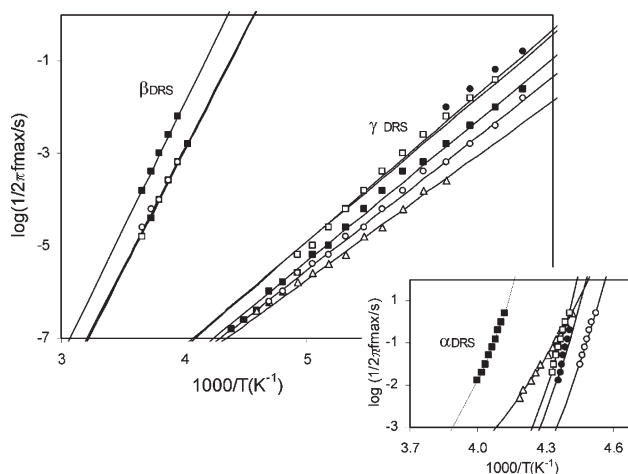


Figure 11 Temperature dependence of relaxation times ($\tau_{\text{max}} = 1/2\pi f_{\text{max}}$). PCL diol (Δ), PUU14 (\blacksquare), PUU23 (\square), PUU32 (\bullet), and PUU40 (\circ). Solid lines represent the Arrhenius fit for the secondary relaxations. The inset shows in more detail the region for the main α_{DRS} -relaxation.

Bogdanov et al.⁹ observed a decrease in the crystallization on poly(ester urethane) samples, mainly with a molecular weight less than 4000 and seems to vanish with increasing length of the block.

The glass transition temperature of PUU14 (-48°C), is higher than in the rest of the PUUs, while the increment of the heat capacity in the transition is smaller (Table I), since a fraction of the PCL blocks pertains to the crystal phase and does not contribute to the glass transition process. This feature is confirmed by dynamic mechanical and dielectric results that also show an increase of the temperature of the α relaxation and a decrease of the intensity with respect to PUUs with higher content of hard segments. The effect of the proximity of the hard domain can hinder the cooperative motions of the amorphous chains producing an increase of the glass transition temperature with respect to the fully amorphous polymer. Nevertheless, it must be noted that the glass transition of PCL-diol is -68°C , and the crystalline fraction is higher than in PUU14. The great difference in T_g must be ascribed to some degree of miscibility in the amorphous phase between the hard and the soft segments. There are no conclusive results supporting phase separation in the amorphous phase between hard and soft segments since the aggregates observed in AFM phase pictures should correspond to the crystalline domains of PCL.

The behavior of samples with 23% or more weight fraction of hard segments is completely different to that of PUU14. Samples cooled from the melt are completely amorphous. Phase separation between hard and soft segments is clearly observed in AFM pictures. Only the glass transition corresponding to the soft segments is observed in DSC thermograms in the same temperature range as PCL-diol. This means that the PCL blocks into copolymer chains can aggregate to form domains larger than the length of cooperativity at the glass transition, which is expected to be on the order of some tens of nanometers. Both the glass transition temperature and the temperature of the α relaxation measured using DRS or DMA techniques decrease with increasing content of hard segments. This cannot be explained by partial miscibility or interphase phenomena since in both cases an increase of the glass transition should be expected in these polymers. A decrease of the glass transition temperature has been found in some amorphous polymer confined in nanometric three-dimensional domains^{34–36} and one can speculate that the dispersion of the PCL phase in nanometric domains dispersed between the hard segment blocks could produce the decrease of their glass transition temperature. The increment of the heat capacity in the glass transition and the intensity of the α relaxation decrease as the crystalline fraction

of PCL decreases in PUUs as it should (Table I and Figs. 6, 8, and 9).

There is a significant difference from the first to the second heating DSC scans. The last step in polymer synthesis is casting from a solution and thus the PUU obtained have crystallized from solution. In the first heating scan a small endothermic peak is shown by the samples with hard segments content equal or above 23% which means that crystallization of PCL chains is still possible in these samples. On the other hand, the broad endotherm shown between 40 and 120°C by the polyurea sample synthesized as a representative of the behavior of the hard segments also appears in the first scan of the PUU40 sample, which means that crystallization of hard blocks is also possible but only when is crystallized from solution, since this peak is completely absent in the second DSC heating scan.

There are no significant differences in the glass transition temperature of the soft segment phase from the first to the second heating scans although the value of the heat capacity increment at the glass transition is lower in the first scan due to the higher crystallinity.

The dynamic-mechanical experiments show the main, α_{DMA} , dynamic mechanical relaxation as a broad loss tangent peak [Fig. 6(b)] whose composition dependence has been already commented on above. At higher temperatures the samples show a broad elastomeric plateau covering the temperature interval between -30 and 40°C . The value of the elastic modulus in this region is characterized by the reinforcing effect of the PCL crystals in the case of PUU14, the sample that present the highest plateau modulus, and that of the hard segment blocks in the other compositions. In the absence of PCL crystallization, clearly the plateau modulus increases as the hard segment fraction does. Chain connectivity between soft and hard segments makes it so that when phase separations takes place, the stiff urea-urethane block domains acts as crosslinking points for the rubbery PCL phase and are responsible of the elastomeric behavior of the polymer. In addition hard blocks act as a filler of the PCL phase.³⁴ Above 60°C , the PUU14 sample collapses due to the melting of the crystalline phase, whereas in the rest of compositions, the elastic modulus decreases smoothly when temperature increases, showing no more transitions in the experimental temperature interval.

Mechanical properties at large strains are a consequence of the copolymer structure. At room temperature, PUU14 shows the characteristic behavior of a stiff semicrystalline polymer, with an elastic modulus around 1 MPa. These properties are desire for the engineering of soft tissue mainly as elastic scaffolds.

After yield and neck formation strain follows with constant stress until break at moderate deformation. The rest of PUU samples show an elastomeric behavior, deformation at break attains 750% in samples PUU23 and PUU32 decreasing for the highest hard segment content. The increase of the elastic modulus with HS content above 23% agrees with the behavior found with DMA measurements.

CONCLUSIONS

The PUUs synthesized in this work are promising materials for biomedical applications in which high elastic deformations are required. The introduction of the Putrescine segments as chain extender allow for modifying the mechanical properties of PCL, which is a material well-known in biomedical applications, to produce a deformable amorphous material. The degradation properties of the polymers are expected to be quite different as well. PCL is a material that degrades hydrolytically at very low rates because of its hydrophobicity, which hinders the access of water molecules to the polymer chains and also because of its crystallinity. Hard block domains impede on the one hand the crystallization of PCL chains but also may allow some hydrogen bonding that is expected to improve water sorption of the material.

The mechanical behavior of the materials can be modulated by varying the fraction of hard segments to yield elastomers that can deform up to 750%. In samples containing more than 20% hard segments, they seem to play the role of crosslinking PCL amorphous blocks acting as reinforcing filler at the same time. On the contrary hard segment contents below 20% allow for PCL segments crystallization and the mechanical behavior is completely different at the other polymers of the series.

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