Synthesis, Characterization, and Chemical Degradation of Segmented Polyurethanes with Butylamine for Chemical Recycling

Abderahmane Elidrissi,[1] Ouassini Krim,[1] Samir Ouslimane,[1] Mohamed Berrabeh,[1] Rachid Touzani[1,2]

[1]Laboratoire de Chimie Appliquée et de l'Environnement. Département de Chimie, Faculté des Sciences, Université Mohammed Ier 60000 Oujda, Morocco
[2]Université Mohammed Ier, Faculté Pluridisciplinaire Nador, B.P.300 Selouane, 62700 Nador, Morocco

ABSTRACT: Polyurethane elastomers (PU) have been synthesized from polytetramethylene glycol 2000 (PTMG 2000); 4, 4'-diphenylmethane diisocyanate (MDI) and 1, 4-butanediol (BD) as chain extender. This synthesis has been done in two steps known as prepolymer methods. The concentration of soft segments and hydrogen attachment in the matrices, have been studied. The results show that the glass transition of the soft segment $T_g(s)$ do not take any changes with the concentration of the soft segment in the matrices. Although, the glass transition temperature of the hard segment $T_g(H)$ increases when the concentration of the hard segment increases in the matrices. In general, the properties of the polyurethane elastomers depend on the extenders nature, the synthesis methods, phase segregation etc. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1623–1631, 2007

Key words: poly(ether urethane)s; thermal properties; chemical recycling; aminolysis

INTRODUCTION

The nonbiodegradabilty of most plastics has caused many environmental problems associated with their disposal. Plastics possess many properties, such as water resistance and long life that make them perfect candidates for packaging. It is therefore not surprising that plastics are used for both consumer and industrial products. Unfortunately, the properties that make these products suitable for packaging also are the major cause of the environmental problems. Accumulation of the used packaging materials in the environment and its concomitant contamination are the inevitable consequences of this process. From this standpoint, the further development of so-called civilization may lead to a sad result: humankind will find itself in a big dump.[1] The annual amount of polymeric wastes continued to increase dramatically each year. The choices for dealing with this waste are limited as incineration of plastic polymers invariably results in the generation of toxic emissions. The only viable solution is to bury the material in landfills. However, this approach is also limited because of the difficult problem of finding available burial sites and for the resistant nature of the petrochemical plastics to biological degradation.[2]

Recycling is an environmental attractive solution; however, only minor portions of plastics are recyclable. Plastic wastes would be recycled by means of retro polymerization (chemical recycling) to monomers and their reuse as plastics should be the primary solution to this problem, since this would conserve large amounts of manufacturing energy, which are inherited in the waste plastics. Moreover, retro-polymerization is advantageous because it can reproduce virgin plastics, and such well-known methods (hydrolysis, glycolysis, amidolysis, aminolysis, etc) have been proposed for the chemical recycling.[3–11] Many studies[12–22] have been concentrated on some polymers, containing reactive polar groups in the main chains, polyamide 6 (PA-6), polycarbonate (PC), polyethylene therephthalate (PET), poly(ε-caprolactone) (ε-PCL), etc. Some patents[23–26] have reported an improve process for increasing the quality of the products and lowering recycling cost.

Polyurethanes have been widely used industrially because of their versatile properties.[27,28] Some of them have been used as biomaterials because of their good biocompatibility, even though, their biodegradation rates largely depend of their chemical structures.[29] To solve the degradability problem, many research efforts have been done. The relationship between the chemical structure of the polyurethanes
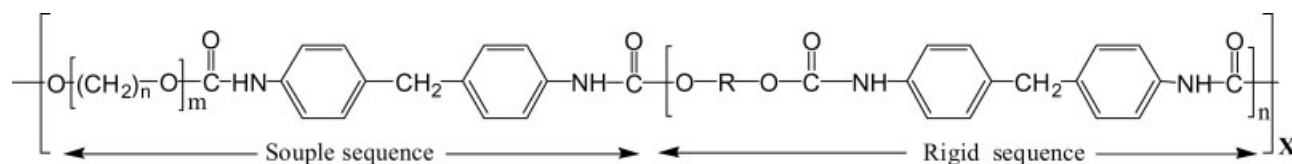
Structure of segmented linear polyurethanes with R = -(CH$_2$)$_4$-

Scheme 1

and the degradation ratio under composting conditions has also been studied.[30–32] It has been concluded that hydrolytic and enzymatic degradation decreased with an increase of the polyester chain length, but increased by substituting aromatic diisocyanates with aliphatic diisocyanates, also the biodegradation was more efficient in polyurethanes prepared from aliphatic diisocyanates than those obtained from aromatic diisocyanates. It was also noted that the degradation of polymers usually decreases with increasing their molecular weights, but the mechanical properties were not satisfied when the molecular weights are too small.[33–35] Troev et al.,[36–38] have reported on the chemical degradation of microporous polyurethane elastomers by some phosphonated compounds [dimethyl phosphonate, diethyl phosphonate, tri(1-methyl-2-chloroethyl) phosphate or triethyl phosphate]. The products formed could be used in the preparation of polymers, including polyurethanes with reduced flammability, improved adhesion, and improved resistance against UV radiation. Kacperski and Spychaj[39] have also used a product derivative from the chemical degradation of polyethylene terephthalate (PET) with triethanolamine as a macrodiol component for rigid polyurethane foam synthesis.

In this study, polyurethane products were synthesized by adding 1,4-butanediol (BD) as chain extenders to prepolymers obtained from polytetramethylene glycol 2000 (PTMG 2000) and 4,4′-diphenylmethane diisocyanate (MDI). We now report in this paper, the synthesis, some general properties of the polyurethanes obtained and we present also preliminary results describing a method of a retro-polymerization (chemical degradation) based on aminolysis. Such process

can be carried out repeatedly without substantial waste.

EXPERIMENTAL

Materials and reagents

The (PTMG 2000) was a product of Dupont de Nemours commercialized under the name of TERATHANE. About (MDI); (BD) and butylamine are commercial available. The solvents were used without further purification. Others chemicals reagents used were analytical grade purchased from Aldrich.

Synthesis

The synthetic route to the segmented polyurethanes is shown in (Scheme 1) employing the general known procedure. For example, PTMG 2000 (1 mol) was dried at 120°C for 24 h in a reaction flash, followed by the addition of MDI (×mol). After the mixture was reacted in the presence of dibuthyltin dilaurate (0.02 wt %) under a nitrogen atmosphere for 3–4 h and (×–1 mol) of BD was added as a chain extenders. The mixture was allowed to react further until the isocyanate peak in an IR spectrum at 2270 cm^{-1} disappeared. The resulting product was precipitated in methanol, filtered, and dried in a vacuum oven at 60°C for 24 h and designated as PU.

Characterizations

The chemical structures of segmented polyurethanes were confirmed by IR and ^{1}H-NMR spectra obtained with a Beckman IR 398 Infrared Spectrophotometer

TABLE I
Average Molecular Weights and Thermal Properties of PU Materials with Different Percentages in Soft Segments

PU nature	%SS	$\overline{Mn}$ (g/mol)	$\overline{Mw}$ (g/mol)	I	$T_g(S)$°C	$T_m(S)$°C	$T_g(H)$°C	$T_m(H)$°C
-PTMG 2000	100	2000	″	″	″	18	″	″
-(PTMG 2000+MDI+BD)n	80	18,000	71,700	3.9	−74.5	18	–	190
-(PTMG 2000+MDI+BD)n	70	16,000	34,800	2.2	−74.3	18	–	190
-(PTMG 2000+MDI+BD)n	60	16,500	27,500	1.7	−74.1	18	–	190
-(PTMG 2000+MDI+BD)n	50	12,000	19,200	1.6	−74.2	18	87	190; 200
-(PTMG 2000+MDI+BD)n	30	3800	13,800	1.6	−73.5	18	87	180; 200; 225

TABLE II
Conditions for the Retropolymerization of Segmented PU by Butylamine

Butylamine(g)	Temp. C°	PU (g)	Duration of degradation (h)	Reacted butylamine (g)	Unreacted butylamine (g)	Degree of degradation%	Yield(g)
5	120	3	4	2	3	60	5.1
5	120	3	12	2.2	2.8	80	5.2
5	120	3	24	2.4	2.6	100	5.5

and Bruker AC 250 MHz Spectrometer, respectively. Ether films or KBr pellet was used to conduct IR spectroscopy in the range of 4000–400 cm^{-1}. The number and the weight average molecular weights ($\overline{Mn};\overline{Mw}$) of these polymers were determinated with size exclusion chromatography (SEC) and their thermal transitions were measured with Differential Scanning Calorimeter (DSC).

Thermal analysis

A Perkin–Elmer DSC4 DSC calibrated with indium was used to evaluate the samples heat transitions. Circular samples with average weights of 10 mg were used for the measurements. The samples were scanned at a heating rate of 10°C/min under dry oxygen free nitrogen flowing at a rate of 50 mL/min. The samples were scanned from (−100 to 200°C), cooled at a rate of 40°C/min, and scanned a second time to 240°C.

SEC

The polydipersity, the weight average and number average molecular weights of polyurethanes were assessed from SEC carried out on a Waters molecular GPC system consisting of a 510 pump, an injector and the 410 refractive index detector (Waters Corp., Milford, MH), the columns were linear 10^5, 10^3, and 10^2 Å, maintained at 30°C (Waters Styragel). Polysty-rene standards with molecular weights in the range of 1500–920,000 were used for calibration. The tetrahyrofurane (THF) was used as eluant with a flow rate of 1.0 mL/min. The data were evaluated using the waters Maxima 820 software package and the results were presented in Table I.

Aminolysis degradation

Retro polymerization experiments were carried out with a three-necked flask equipped with a stirrer, thermometer and reflex condenser. About 2 g of segmented polyurethane elastomers were dissolved in the mixture of dimethyl formamide and toluene, then we added an excess of butylamine. The mixture was stirred to reaction temperature (120°C) by use of an oil bath. After the desired time, the samples were cooled to room temperature after which any precipitation formed was filtered off. The solvent was removed by rotary evaporation and the unreacted butylamine was removed under vacuum. The retro polymerization products were characterized by IR and NMR spectroscopy and the results are presented in Table II.

RESULTS AND DISCUSSION

Segmented polyurethanes were prepared in a polar solvent to avoid the phenomenon of macroseparation of phases. The synthesis was realized in two
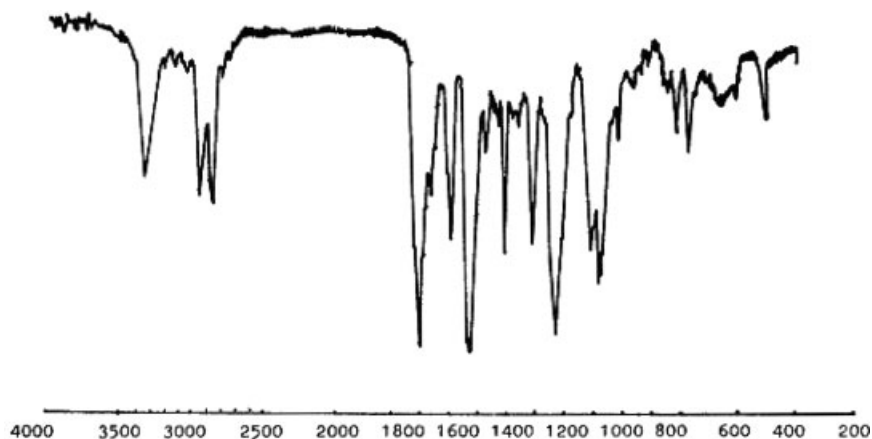

Figure 1 Infrared spectrum of segmented polyurethane elastomers from PTMG 2000; MDI and BD were measured in DMF solutions.
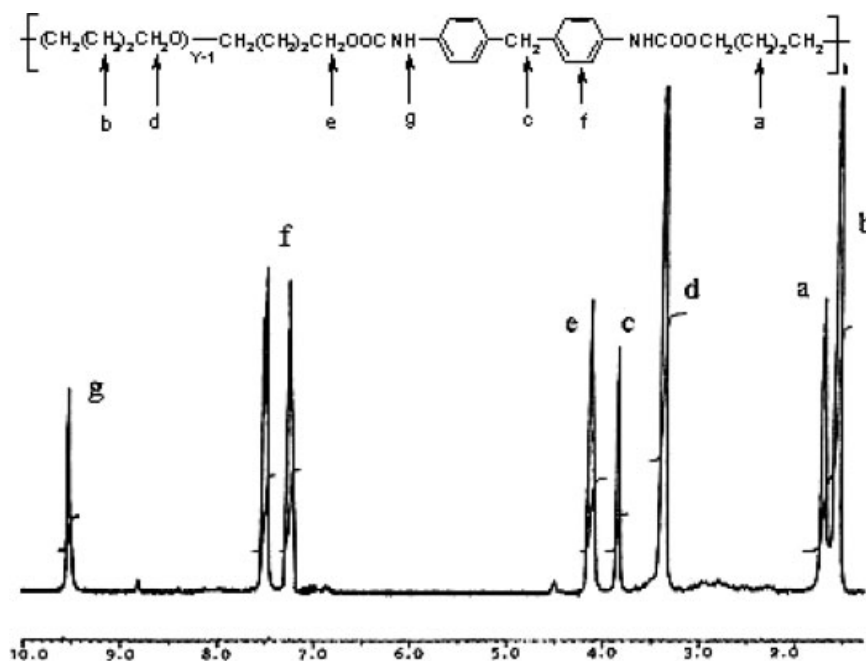
Figure 2 Proton NMR spectrum of segmented polyurethane elastomers (PU) from PTMG 2000; MDI and BD.

stages, first a prepolymer in NCO extremity was obtained, then reacted with a chain extenders in a second stage. During the reaction a light disorder appears since the addition of chain extenders to the initially transparent solution, this phenomenon could result from a segregation of phases in the material. These materials were synthesized from PTMG 2000 as a soft sequence bounded by urethane bridges to hard sequence $\sim$(MDI-BD)$\sim_{n'}$ composed of MDI and BD.

The rate of flexibility defined by using the joint definition: Weight of macrodiol (m_d) divided by the total mass (m_t) of reagents %SS $= \frac{m_d}{m_t}$ varies from 80 to 30%. The general structure of segmented PU is represented in Scheme 1.

This synthesis was followed by IR (Fig. 1), the NCO groups in MDI and the OH groups in PTM-2000 appear, at about 2270 cm^{-1} and 3500 cm^{-1}, respectively, but they have been disappeared totally in the IR spectrum of PU prepared. New bands appeared at about 3400 cm^{-1}, 1705 cm^{-1}, and 1050 cm^{-1}, which have been assigned respectively, to v(NH) vibration, v(C=O) carbonyl groups from urethane that are hydrogen bonded and urethane ether groups v(CO—O—C) vibration. This result indicates that the polyaddition was complete. Furthermore, the absorbance at 1110 cm^{-1} was attributed to the vibration of ether bonds in PTMG 2000 v(C—O—C). The band attributed to the NH stretching mode appears at 3400 cm^{-1}, corresponding to the frequency for the nonassociated mode. It may indicate that hydrogen bonding of urethane groups is dissociated in solution. Therefore, the 1705 cm^{-1} band can

be assigned mainly to the associated C=O stretching mode. Thus, it may be thought that the urethane C=O groups are associated with hydrogen bonding in (DMF).

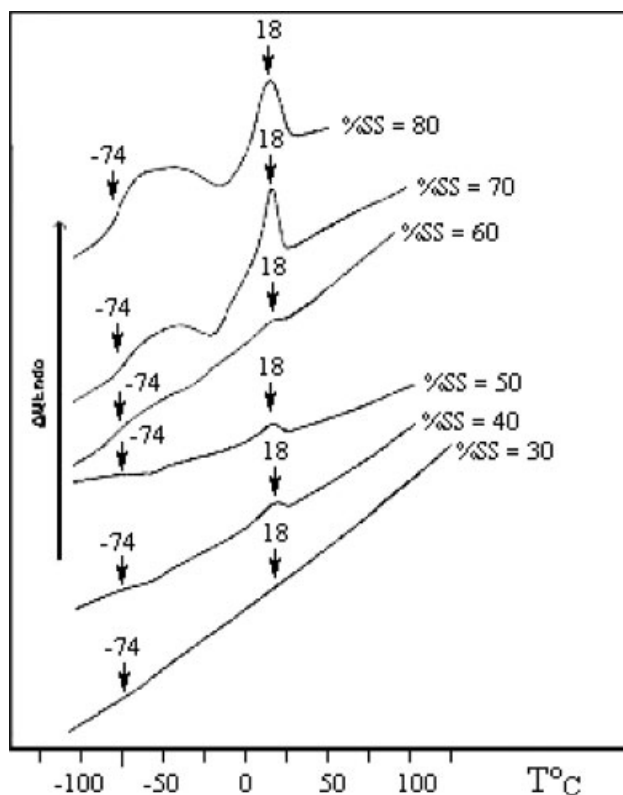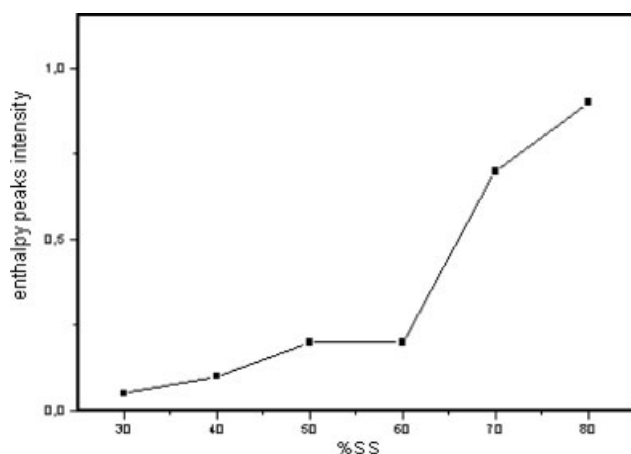**Figure 3** DSC Thermograms of segmented PU variation with %SS; [−100, +120°C].

Figure 4 Intensity enthalpy peaks variations on the flexibility level.

The segmented linear polyurethanes obtained are soluble in typical solvents such as DMF, DMA, THF, or CHCl$_3$. Figure 2 shows that, the proton NMR resonance signals are ranged between of 1.60 and 9.60 ppm. The average molecular weights, polydispersity, and thermal properties [glass transition (T_g) and melting transition temperatures (T_m)] of polyurethanes are estimated with SEC and DSC, respectively (Table I).

The obtain average molecular weights values ($\overline{Mn};\overline{Mw}$) of the segmented polyurethanes were given compared with a calibration curve from polystyrene standards. We noticed in general that their average molecular weights decrease when the level of soft sequence (PTMG 200) contained inside these macromolecules decreases too. This suggests, that values of molecular weights depend on both the molecular weights of soft and hard segments and their concentrations determined again by molecular ratios. Therefore, the molecular weights of the repeating unit increase with increasing PTMG segment composition. The values of the polydispersity index (I) obtained are similar to the theoretical values. The value $I = 3.9$ obtained (Table I, entry 2) is not unusual. It might be due to the synthesis conditions and to the thermal treatment to which these samples were subjected after preparation. The polydispersity index (I) in entry 5 and 6 are relatively low, possibly resulting from the solubility problems in PU with high hard segment concentrations.

DSC thermogram of the pure PTMG 2000 shows a sharp melting temperature (T_m) toward 18°C, the T_g may be masked because of its high crystallinity. For the PU materials, we noticed that the position of the melting point of the soft sequence $T_m(s)$ does not vary according to the level of flexibility contained, but the intensity of the enthalpy peaks decreases as the flexibility level decreases too (see Fig. 3). This phenomenon is not only because of the reduction of

the amounts of the PTMG 2000 in the material, but also to the clear phase segregation in the material. On the other hand, a better organization of the hard sequence is noted; this result is in agreement with those mentioned in the literature.[40] The dependence of T_m and intensity of enthalpy peaks on the flexibility level is shown in Figure 4.

DSC thermograms of the PU also show an endothermic variation toward the lower temperatures corresponding to the glass transition temperature of the soft sequence $T_g(s)$ rich in PTMG 2000, this value does not exhibit a great variation (−74 and −72°C) according to the level of flexibility, because the size of the polyether PTMG 2000 was kept constant all the synthesis (Fig. 3). In contrast, the $T_g(s)$ variation of the soft sequence is rather broad when the size of the polyether was varied, keeping the hard sequence size constant. These results are in agreement with those reported in the literature.[41–43] In general; the chain ends of the soft sequences have a reduced mobility because of their chemical attachments with the hard sequences of the macromolecules. We can conclude that when the average molecular weight of macrodiol (PTMG) decreases, the phase segregation is attenuated and the material tends to present only one morphological phase. The phase miscibility can be caused by the interactions through hydrogen bonding of NH urethane with the oxygen of the bridge ether in the soft sequence. Generally, this type of compounds presents a micro-phase separa-
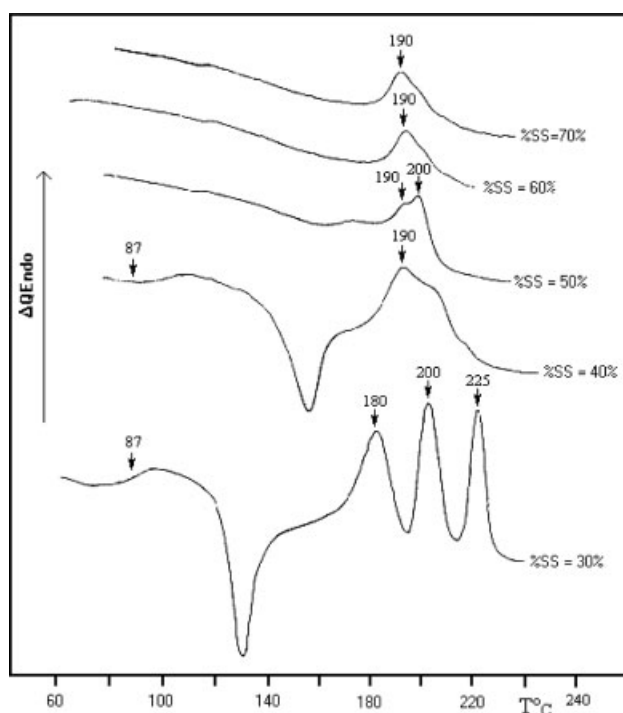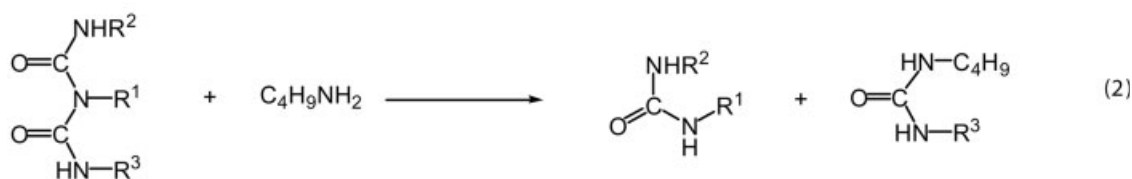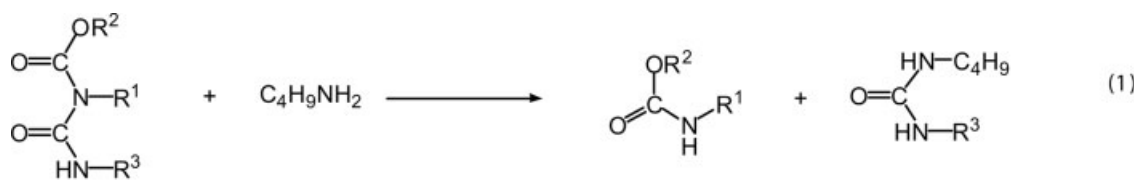

Figure 5 DSC Thermograms of segmented PU; [60 to 250°C].

Degradation of allophonate and biuret groups by butylamine

Scheme 2

tion. Inversely, when the PTMG $\overline{Mn}$ grows, the influence of the hard sequence decreases taking along the $T_g(S)$ values toward the lower temperatures, the degree of the mixer between the two segments decreases and the phase separation increases and a macro-phase separation is approached.

Segmented polyurethanes having a level of rigidity $\leq 30\% \approx$ (%SS ≥ 70), don't show clearly the phenomena corresponding to the $T_g(H)$ and $T_m(H)$ of the hard sequence specially at the time of the second scanning (Fig. 5). This behavior might be assigned to the quantities of hard sequences with short lengths present as impurities in soft domains, which in theory were only formed by two units of MDI. These short sequences do not have the time to crystallize at the time of increasing temperature at 20°C min^{-1} or at 10°C min^{-1}. This may also due to an increase of incomplete crystalline phase due to the phase mixing between the hard and soft sequences. This result is similar to those reported in the literature.[40,44,45] Different $T_m(H)$ values have been observed with a level of rigidity (70%) $\approx$ (%SS = 30), this suggests the presence of the different crystalline structures in these compounds.[46] Many factors influence these transitions, such as hard sequence crystallization, thermal history of the sample and phase segregation.

## Degradation of segmented linear polyurethanes

Okuto et al.,[47] with action of butylamine have transformed the allophonate groups to urethane and urea bonds (1) similarly; the biuret groups have also been transformed to urea bonds (2) (Scheme 2).

We try to use the similar procedure to degradate the PU materials based on MDI, PTMG 2000 and BD (Scheme 1). Some segmented polyurethanes were dissolved in the mixture of DMF/toluene and were subjected to degradation by butylamine at 120°C for different periods. After the desired time, the reaction mixture of DMF/toluene and the unreacted butylamine were removed by vapor rotary and under vacuum, respectively. The products resulted from the degradation are soluble in CHCl$_3$, CH$_2$Cl$_2$, THF, DMF, etc. It has been found that when heating polyurethane elastomers with butylamine at 120°C during 24 h, the polyurethane elastomers degrades totally (Table II).

The ^{1}H-NMR spectrum of the virgin polyurethane elastomers (Fig. 2) shows specially signals at 9.50 ppm (g) and 4.20 ppm (e) corresponding, at proton binding aromatic urethane and at methylene groups in α position of urethane, respectively (Scheme 3).

Although, the ^{1}H-NMR spectrum of the degraded products after 24 h heating at 120°C shows news signals at 8.48 ppm and at 6.20 ppm (Fig. 6) corresponding to —NH— urea attached to aromatic part and to —NH— urea attached to aliphatic part, respectively (Scheme 4).
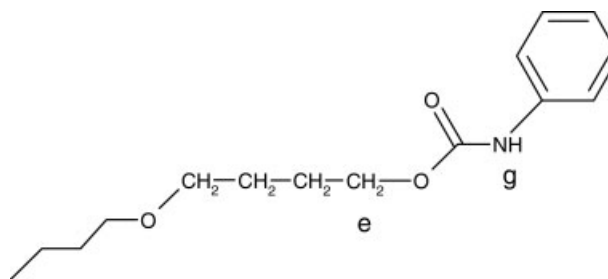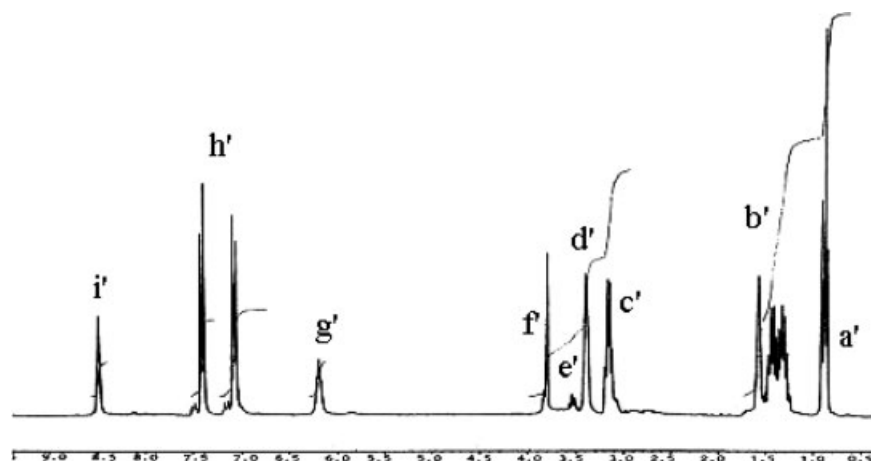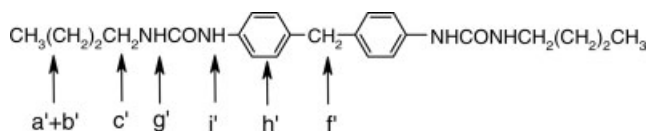

Scheme 3

Figure 6 ¹H-NMR spectrum of degraded products from segmented polyurethane elastomers.

Furthermore, a new signal has appeared at 3.10 ppm (c′) corresponding to methylene group (—CH₂) in α position of aliphatic urea. It was also observed in the proton NMR spectrum (Fig. 6) that signals at 9.50 (g) and 4.20 ppm (e) assigned, respectively, to the proton of —NH— aromatic urethane bond and to methylene groups in α position of urethane bond have been disappeared completely. These data confirm absolutely in one hand the degradation of urethane bonds and in the other hand the formation of new urea bonds. Furthermore, we have also remarked in the spectre of the degraded products (Fig. 6) others signals at 1.60 ppm (b′), 3.40 ppm (d′) and 3.56 ppm (e′) which represent methylene groups of PTMG in different positions, respectively (Scheme 5).

The most important signal was at 3.56 ppm (e′) which may be assigned to the methylene groups in α position from the hydroxyl bonds in the PTMG structure. The integration of this signal can be used for the determination of number average molecular weight of the soft sequence (PTMG). The IR spectrum of the sample degraded in butylamine media is presented in Figure 7, and shows clearly intense peak corresponding to urea carbonyl at 1640 cm⁻¹ ν(—NH—co—NH—). We have also noted that ν(C=O) carbonyl groups from urethane that are hydrogen bonded has disappeared.

Furthermore, in the range of 3600–3300 cm⁻¹, there are broad band vibrations, which may be resulted from ν(OH) and ν(NH) urea bonded. There is no evidence of the disappearance or decrease in intensity peak at 1110 cm⁻¹ assigned to (C—O—C—) group vibration in PTMG segments. Moreover, the peak at 1600 cm⁻¹ due to the aromatic stretching was clearly observed in the virgin material and its intensity decreases in the degraded products. A small shoulder peak appears at 3100 cm⁻¹, which may be attributed to the vibration of —NH primary amine, excess of butylamine noneliminated from the media. The presence of peak at 1106 cm⁻¹ in the spectrum of the degraded products with the same intensity as in the virgin polymer indicates that ether groups in the main chain of the soft sequences of PTMG 2000 were more resistant to significant aminolysis (see Table III).[48,49] The resistance of ether groups in the soft segment to degradation is possibly because of the coexistence of hydrocarbon polyol and PTMG 2000 as a large soft segments, and also due to the entrapment of these soft segments in the virtually crosslinked hard segments domains.

The IR spectroscopy is particularly useful to detect modification and/or formation of new chemical bonds by a degradation process. However, information on phase separation might be difficult to obtain in the presence of chemical degradation, because the appearance of new bonds could overlap with polyurethanes IR absorptions normally sensitive to phase separation. In addition, these new bonds, which are

Scheme 4 Degraded product resulted from PU.
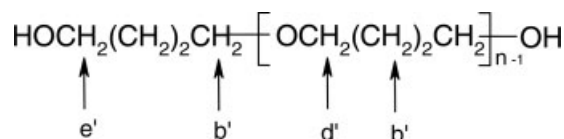
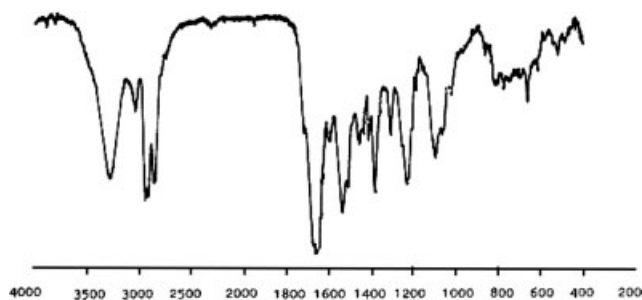**Scheme 5** Product resulted from degradation phenomenon of PU.

Figure 7 Infrared spectrums of degraded product solutions from PU.

attributed to degradation products, are summarized in Table III with the possible attributions.

Degradation mechanism of polyurethane elastomers by butylamine

The results obtained show that degradation mechanism of segmented polyurethanes by butylamine includes two simultaneous reactions (Scheme 6).

1. Breaking reaction of the urethane bonds.
2. Formation of urea bonds by alkylation.

The preferential formation of degradation product A as shown in Scheme 6, was confirmed, by proton NMR and IR spectroscopy of the crude product in the stage of the aminolysis of PU, respectively. This result supports the selective aminolysis of the urethane groups and not the ether groups during the degradation. The degradation mechanism proposed,
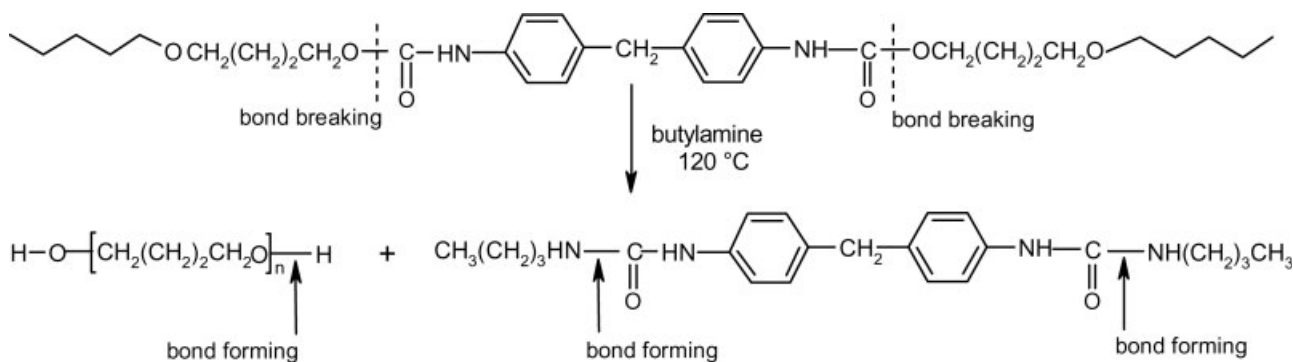
which lead to urea and alcohol groups appear more acceptable in our conditions.

CONCLUSIONS

In summary, first polyurethanes containing 4,4′diphenylmethane diisocyanate and polyether (PTMG 2000) as soft sequences were synthesized, and were characterized by proton NMR and IR spectroscopy. Theirs number and weight average molecular weights were obtained by SEC. The thermal properties (glass transition temperature -T_g-; melting transition -T_m-) were studied and discussed with the level of flexibility in PU. It was noted that the glass transition temperature value of the soft segments -$T_g(s)$- does not change when the level flexibility of the polyurethanes changes too. The studies on accelerated chemical recycling (retro polymerization) of PU by aminolysis without any catalysts revealed significant deterioration of urethane bonds and formation of novel urea bonds. However, the ether groups in the main chain of polyether (soft sequences) were more resistant to the retro polymerization. Data from proton NMR and IR spectroscopy, confirm the formation of the above-mentioned structures during the degradation of flexible polyether polyurethanes. Even, the polymer containing PTMG has showed no evidence of disappearance or reduction of peak intensity of ether group in soft sequences (PTMG). This study reveals that increase in temperature and time of aminolysis can greatly enhance the degradation rate, and will help to understand what type of reaction is taking place predominantly at what temperature. This may open up a new way to recycle

TABLE III
Characteristic Absorption Bands in the IR Spectrum of Segmented PU and Degraded Products

Material	Wave number	Relative intensity	Main assignments (a)
PU	3400	m	ν (N—H) free in urethane group
	3320	m	ν (N—H) H-bonded (associated)
	2920	vs	ν (CH$_2$)$_{PT}$ Polytetramethylene glycol
	2840	vs	ν (CH$_2$)$_{PT}$ Polytetramethylene glycol
	1705	m	ν (C=O) H-bonded Carbonyl from urethane group
	1600	m	—C—H in C$_6$H$_4$; ν (C=C) ground
	1520–1500	sh	δ (N—H)$_{UT}$ + ν (CN)$_{UT}$
	1370	s	ω (CH$_2$)$_{PT}$
	1230	sh	δ (N—H)$_{UT}$ + ν (CN)$_{UT}$
	1110	vs	ν (COC)$_{PT}$
Degraded products	3600–3300	m	Broad ν (O—H) and/or ν (N—H)
	3100	vw	Primary amine ν (N—H)
	2920	vs	ν (CH$_2$)$_{PT}$ Polytetramethylene glycol
	2840	vs	ν (CH$_2$)$_{PT}$ Polytetramethylene glycol
	1640	vs	ν (C=O), Urea
	1600	m	ν (N—H Primary amine)
	1548	sh	δ (N—H)$_{UA}$ + ν (CN)$_{UA}$
	1240	sh	δ (N—H)$_{UA}$ + ν (CN)$_{UA}$
	1110	vs	ν (COC)$_{PT}$

Scheme 6 Degradation mechanism of PU elastomers by butylamine.

the above degradable polymers with varied structures. The degraded products, directly or after chemical treatments can be used for the preparation of polymers or as chemical industrial reagents.

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