

Influence of Urethane Group on Properties of Crosslinked Polyurethane Elastomers

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ABSTRACT: Three series of weakly crosslinked polyurethanes based on a hydroxyterminated polybutadiene, hydroxyterminated butadiene–acrylonitrile copolymer, and hydroxyterminated ethylene–adipate–maleate–fumarate copolymer were prepared while varying the hard segment content between 1.72 and 2.36 mol —NH—COO—/1000 g polymer. Information on the microphase structure and the properties of the synthesized polyurethanes was obtained by differential scanning calorimetry, wide-angle X-ray scattering, and mechanical studies. Up to a urethane concentration of around 2 mol —NH—COO—/1000 g polymer, there

is a mixture of hard–hard and hard–soft segments. Above this concentration a large part of the hard–soft segments passes into hard–hard crystallites, liberating the soft segments. The best mechanical properties of the studied polyurethanes were found for a urethane concentration of around 2 mol —NH—COO—/1000 g polymer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1858–1867, 2003

Key words: urethane group; crystallinity; morphology; segregation; mechanical properties

INTRODUCTION

Polyurethane (PU) is a widely used polymeric material with many technical applications.¹ Segmented PUs are block copolymers that are usually composed of a polyether or polyester soft segment and urethane hard segment. The hard segment is formed by extending a terminal diisocyanate with a low molecular weight diol. The hard and soft segments in PU are thermodynamically incompatible and PU undergoes microphase segregation, which has a great influence on the polymer.^{2–6}

The urethane group is strongly polarized, being characterized by high cohesion energy⁷ and the presence of hydrogen bonds.⁸ The concentration of the urethane groups modifies the PU properties. Thus, the resistance at break, the modulus of elasticity, the elastic resilience, and the glass-transition temperature (T_g) increase with increasing urethane concentration whereas the elasticity decreases.^{9–15}

Brunette and coworkers^{16,17} investigated different states of segmented PUs incorporating a hydroxyterminated polybutadiene (HTPB) soft segment. They found that the T_g of the soft segment is of the same order of magnitude as that of the butadiene homopolymer, regardless of the content of the hard segment. This is an indication that a complete segregation

of both the hard and soft segment units occurs. In contrast, the results of this study show that the phase segregation in PU takes place at a well-defined concentration of the urethane group, namely, at around 2–2.2 mol urethane/1000 g polymer.

The aim of this article is to provide further details on the influence of the urethane group on the properties of the crosslinked PU. For this purpose, three series of PUs were synthesized starting from HTPB, hydroxyterminated butadiene–acrylonitrile (HTBN) copolymer, and hydroxyterminated ethylene–adipate–maleate–fumarate (HTEAMF) copolymer. All of these compounds (soft segments in the PU) were reacted with toluene diisocyanate (TDI) as the hard segment. Glycerine was used as the extender. The morphology and the effect of the urethane group on the properties of the PU elastomers were investigated using differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS). In addition, the mechanical properties were determined and discussed in relation to the results of the DSC and WAXS studies.

EXPERIMENTAL

Materials

The HTPB, HTBN, and HTEAMF prepolymers were obtained in our laboratory. The PU elastomers were synthesized starting from HTB, HTBN, and HTEAMF in a reaction with TDI, the last being an 80:20 mixture of 2,4- and 2,6-isomers (Sigma–Aldrich, Deisenhofe,

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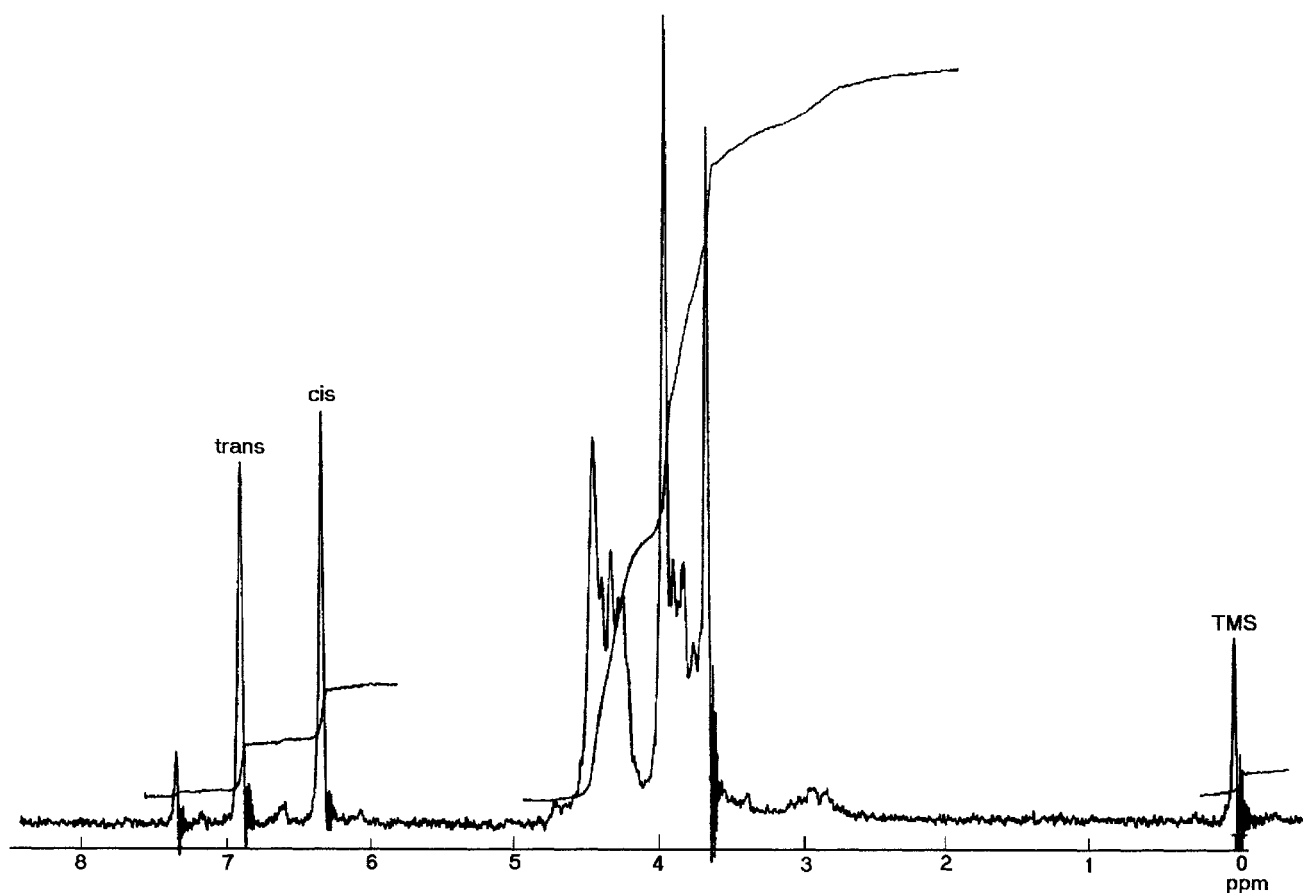


Figure 1 $^1\text{H-NMR}$ of HTEAMF.

Germany). The other compounds used in the present study were analytical grade.

Synthesis of HTPB

HTPB was synthesized by a free-radical polymerization of 10 wt % butadiene in ethanol solution. Oxygenated water with 33 wt % H_2O_2 was used as a polymerization initiator. The molar ratio between the butadiene and H_2O_2 was 5:12. The polymerization reaction was carried out in an autoclave at $117 \pm 0.2^\circ\text{C}$ in the presence of a dry nitrogen atmosphere at a pressure of 17 atm. The resulting prepolymer was distilled to remove ethanol, washed many times with water, filtered, and vacuum dried at reduced pressure.

The synthesized HTPB, which is a colorless high viscous product ($\eta_{\text{CP}} = 62,000$ at 20°C), had a number-average molecular weight of 2800, which was determined from gel permeation chromatography (GPC), and an average functionality between 1.98 and 2.06 hydroxyl groups per molecule.

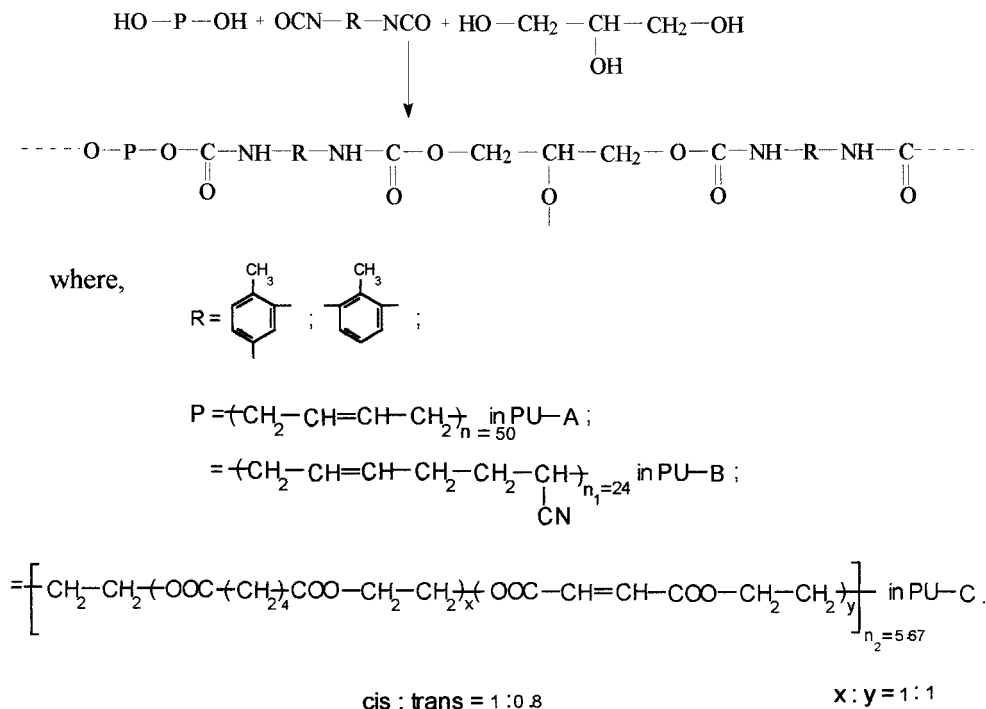
Synthesis of HTBN

The same conditions as those for the preparation of HTPB were used to synthesize HTBN but instead

using butadiene and acrylonitrile (85:15 weight ratio) as the starting monomers. The number-average molecular weight of the synthesized HTBN ($\eta_{\text{CP}} = 85,000$ at 20°C) was 2700, and the average functionality was between 1.95 and 2.08 hydroxyl groups per molecule.

Synthesis of HTEAMF

The HTEAMF copolymer was synthesized by fusion condensation using ethylene glycol (1 mol), adipic acid (0.2 mol), and maleic anhydride (0.8 mol) as the raw compounds. The reaction was carried out at temperatures between 140 and 200°C and a pressure of 1.5 mmHg in the presence of a catalyst based on a stannous oxalate and sodium acetate (1:0.2 weight ratio) mixture (0.1 wt %). Both the oligomers and the catalyst were removed from the reaction system using a solution of HTEAMF (20 wt%) in a benzene/ethanol (1:2 volumes) mixture, which was subsequently precipitated many times with water. The crude product obtained a liquid with very high viscosity was dried under a vacuum at room temperature for 2 weeks. The number-average molecular weight of the synthesized copolymer ($\eta_{\text{CP}} = 96,500$) was 2060, the acidity index was 0.2 mg KOH/g polymer, and the hydroxyl num-



Scheme 1 The synthesis of PU-A, PU-B, and PU-C elastomers.

ber was 54.45 mg KOH/g polymer. The ratio of malate/fumarate (1:0.8 by weight) was determined by means of $^1\text{H-NMR}$ spectroscopy (Fig. 1).

Synthesis of PU

Thermoplastic PU was synthesized by a reaction between the polyols, isocyanate, and glycerine. The polyols were first dehydrated for 2 h at 120°C at a pressure of 2–3 mmHg, after which the temperature was reduced to 60°C . At this temperature the glycerine and TDI were quickly added to the polyol under vigorous stirring for 1–1.5 min, and then the molten sample was degassed at low pressure and poured into a steel mold ($200 \times 200 \times 1.5$ mm). In order to obtain various concentrations of the urethane structures, as well as various degrees of crosslinking for each series of synthesized PUs, the molar ratio of polyol and glycerine was maintained constant (1:7) while the TDI concentration was varied from 8.62 to 11.38 mol. The mold containing the molten PU was placed in an oven at 80°C and maintained for 8 h to finish the polyaddition process.

Characterization

The GPC measurements were carried out by means of a PL-EMD 950 evaporative mass detector (Polymer Laboratories Ltd., Shropshire, UK). Calibration of the apparatus was performed using monodispersing

polystyrene standard samples with a narrow polydispersity (GmbH, Darmstadt, Germany).

The viscosity of the synthesized polymers was determined on a Brookfield type viscometer (Brookfield Engineering Laboratories, Stoughton, MA), which was run at a speed of 6 rpm at 20°C .

The $^1\text{H-NMR}$ spectrum of the HTEAMF copolymer was obtained on a Jeol JNMC-60-HL instrument at 60°C from a DMSO polyol solution.

The IR spectra of the synthesized samples were recorded on an M 80 Specord spectrophotometer using KBr pellets.

The DSC studies were carried out using a Mettler 12E instrument at a heating rate of $2^\circ\text{C}/\text{min}$ with temperatures between -100 and 100°C in a nitrogen atmosphere. The midpoint of the specific heat change was taken as the T_g .

The WAXS analyses were performed on a TUR M-62 diffractometer, coupled with a computer, and

TABLE I
Urethane Content, OH:NCO Molar Ratio, and Crosslinking Degree of Each Series of Synthesized PUs

Sample No.	-NH-COO-(mol)/ 1000 g Polymer	OH:NCO Molar Ratio	Crosslinking Degree (%)
1	1.72	1:0.68	0.00
2	1.84	1:0.75	6.00
3	1.97	1:0.81	29.00
4	2.08	1:0.87	51.00
5	2.36	1:0.99	96.18

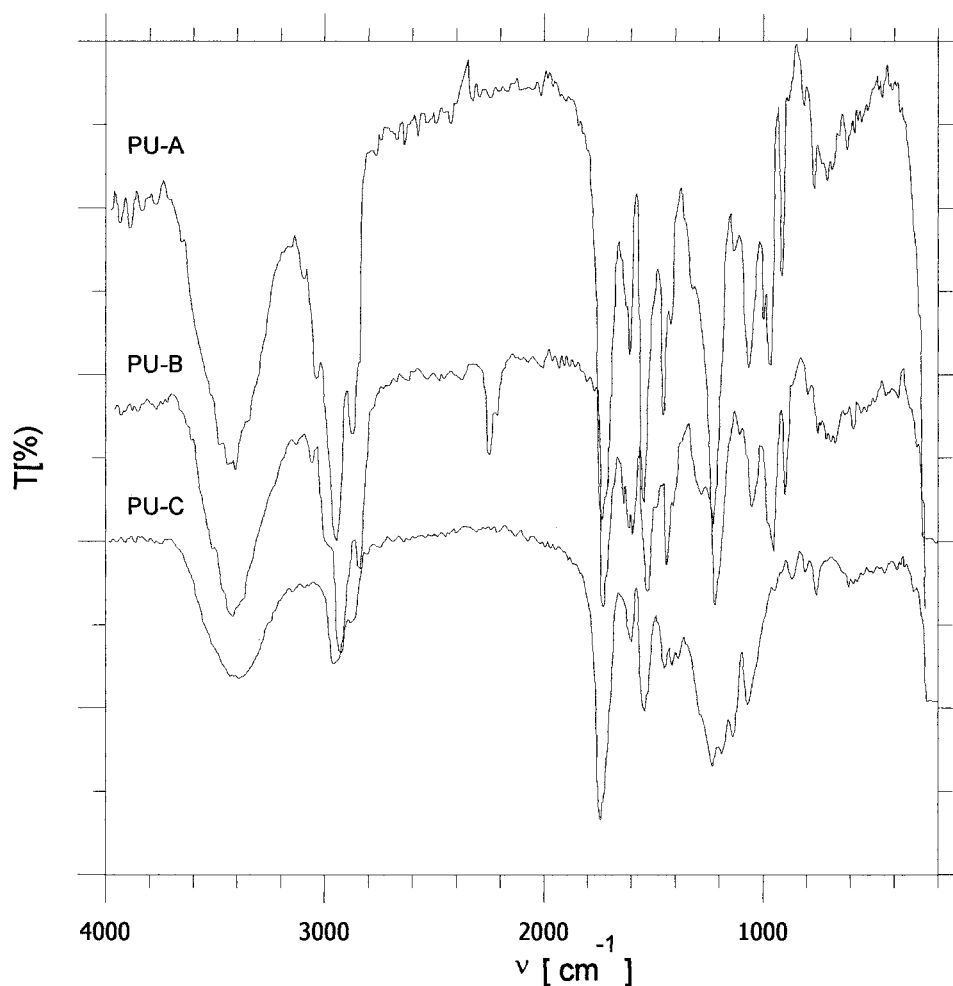


Figure 2 Typical IR spectra of PU-A, PU-B, and PU-C.

Ni-filtered Cu-K_2 radiation ($\lambda = 0.154 \text{ nm}$) was used. The working conditions were 36 kV and 20 mA and a goniometer speed of $0.5^\circ\text{C}/\text{min}$. All the diffractograms were investigated in the range of $4\text{--}40^\circ 2\theta$ at room temperature. The crystalline part versus the amorphous was evaluated using the regression method.

The physicomechanical measurements were carried out at room temperature using a TIRA-TEST-2161 apparatus at a crosshead speed of 20 mm/min.

RESULTS AND DISCUSSION

The PUs (PU-A, PU-B, and PU-C) were obtained starting from HTPB, HTBN, and HTEAMF compounds in a reaction with glycerine and TDI according to Scheme 1.

The degree of crosslinking was varied by changing the ratio of glycerine to diisocyanate as shown in Table I. Using various OH/NCO ratios, it was possible to obtain three series of PUs, PU-A₁₋₅, PU-B₁₋₅, and PU-C₁₋₅, which have degrees of crosslinking between 0 and 96%, according to the added glycerine.

The synthesized PUs were first characterized using IR spectroscopy, and the IR spectra are shown in Figure 2. The main wavenumbers corresponding to the characteristic bands are shown in Table II. The IR spectra of the PUs were interpreted with the aid of methods reported in the literature for analogous groups.¹⁸⁻²⁰

The NH absorption bands for all the synthesized PUs are found at $3440\text{--}3330 \text{ cm}^{-1}$ and methylene group absorption bands at $2962\text{--}2886 \text{ cm}^{-1}$. PU-B can be characterized by the band at 2250 cm^{-1} ($\text{C}\equiv\text{N}$). The IR spectra show typical bands in the carbonyl vibration region ($1776\text{--}1725 \text{ cm}^{-1}$), which are attributed to both the esteric and urethane group ($\text{C}=\text{O}$), and a band at around 1620 cm^{-1} , which is assigned to the $\text{C}=\text{C}$ double bond. The bands indicating the presence of the aromatic ring are the valence vibrations within the $3032\text{--}3048$ and $1602\text{--}1606 \text{ cm}^{-1}$ ranges, and the stretching vibration band is at 820 cm^{-1} . In the $1582\text{--}1550 \text{ cm}^{-1}$ range specific bands can be noted for N—H and C—N groups (amide II). All the studied PUs can be also characterized by the bands between 1176 and 1122 cm^{-1} (C—O—C) that are attributed to the hard

TABLE II
Wavenumber Corresponding to Characteristic Bands in IR Spectra of Synthesized PUs

Wavenumber (cm ⁻¹)			Relative Intensity	Main Assignments
PU-A	PU-B	PU-C		
3440	3446	3426	w, sh	$\nu(\text{N—H})$, free N—H
3329	3330	3330	s	$\nu(\text{N—H})$, bonded N—H
3044	3048	3032	w	$\nu(\text{C—H})$, in aromatic ring
2962	2963	2960	s	$\nu_s(\text{CH}_2)$
2933	2930	2924	s	$\nu_s(\text{CH}_2)$
2880	2889	2886	s, sh	$\nu_s(\text{CH}_2)$
—	2250	—	m	$\nu(\text{C=N})$
—	—	1776	vs	$\nu(\text{C=O})$ in ester bonded with N—H from same urethane group
—	—	1720	vs	$\nu(\text{C=O})$ in ester bonded with N—H from another urethane group
1730	1738	—	vs	$\nu(\text{C=O})$, free C=O
1725	1726	—	vs	$\nu(\text{C=O})$, bonded C=O
1620	1622	1625	w	$\nu(\text{C=C})$, symmetrical
1604	1606	1602	s	$\nu(\text{C=C})$ in aromatic ring
1550	1552	1582	vs	$\delta(\text{N—H})$ and $\nu(\text{C—N})$
1464	1464	1462	w	$\delta(\text{CH}_2)$
1240	1244	1275	s	$\delta(\text{N—H})$ and $\delta(\text{C—N})$
1170	1176	1122	m	$\nu(\text{C—O—C})$ in hard segment
—	—	1118	m	$\nu(\text{C—O—C})$ in soft segment
970	972	974	s	$\gamma(\text{CH=CH})$ in trans
818	820	822	w	$\gamma(\text{C—H})$ in aromatic ring

w, weak; m, medium; sh, shoulder; s, strong; vs, very strong.

segments. The band at 1118 cm⁻¹ (C—O—C), which is characteristic of the soft segment, was found only for PU-C.

DSC analysis

DSC analysis was carried out for the evaluation of the T_g values of the synthesized PUs. Figure 3 shows the

DSC traces for the synthesized PUs and Table III lists the T_g values measured for PU-A, PU-B, and PU-C.

The PU-A and PU-B show a similar variation in the T_g values with the concentration of the urethane group. For a concentration of —NH—COO—/1000 g polymer up to 2.08, the T_g values of both PU-A and PU-B continuously increase then decrease by 5–6°C as the concentration in the urethane groups increases by

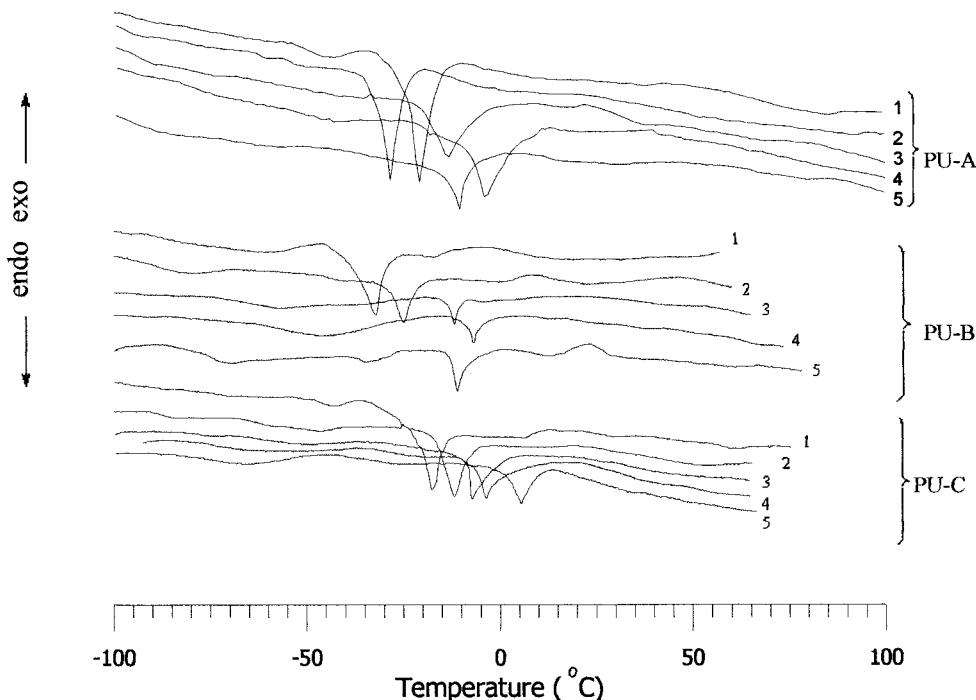


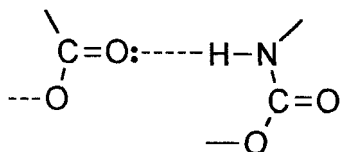
Figure 3 DSC traces of the synthesized PUs.

TABLE III
Glass-Transition Temperatures (T_g) Evaluated for
Synthesized PUs

-NH-COO(mol)/1000 g Polymer	T_g (°C)		
	PU-A	PU-B	PU-C
1.72	-29	-33	-18
1.84	-22	-26	-13
1.96	-14	-12	-8
2.08	-6	-7	-5
2.36	-12	-11	6

0.28 mol. This behavior is not in agreement with the results reported previously by Brunette and coworkers.^{16,17} They studied a series of PUs based on a HTPB compound and found a complete segregation of the hard from the soft segment units, regardless of the hard segment content. Our results indicate the presence of a dissolving process of the hard segments in the soft phase. This process can be associated with the hydrogen bonding interactions between the soft and hard segments.

PU-C exhibits a different behavior in the T_g values as compared to those of PU-A and PU-B, respectively. The T_g values of PU-C continuously increase with the increasing of the urethane concentration. This indicates the presence of strong hydrogen bonds between the ester structures and the urethane groups,²¹ as follows:



These interactions make the phase segregation in PU-C less clear as was observed in PU-A and PU-B. For PU-A and PU-B the decrease of the T_g values starting with a concentration of urethane between 2 and 2.2 mol -NH-COO-/1000 g polymer reveals that above this concentration the urethane groups form ordered and well-defined microcrystalline structures, independently of the presence of the soft segment structures.

WAXS analysis

Figures 4–6 show the results of the WAXS on the PU-A, PU-B, and PU-C, respectively. In every WAXS diagram two of the distinct crystal structures, type I and type II, occur in the mild crystallization conditions that were used.²² The type II crystal structures are more ordered than the type I structures.

The curves in Figures 4–6 were used to evaluate the crystallinity index (α_x) as the ratio of the area under

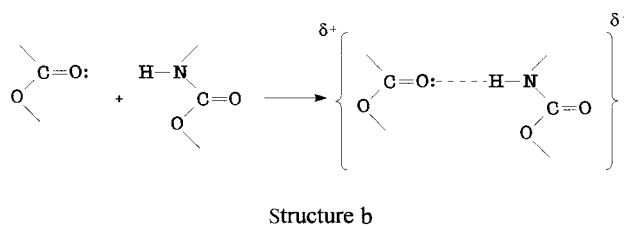
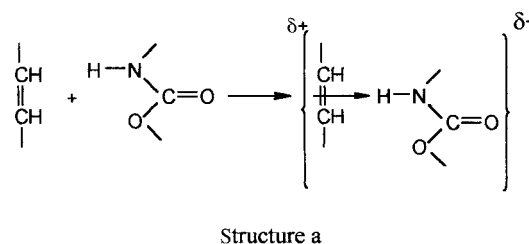
the crystalline pattern (ΣA_{cr}) to the total scattering ($\Sigma A_{cr} + \Sigma A_{am}$) of the original pattern:²³

$$\alpha_x = \frac{\Sigma A_{cr}}{(\Sigma A_{cr} + \Sigma A_{am})}$$

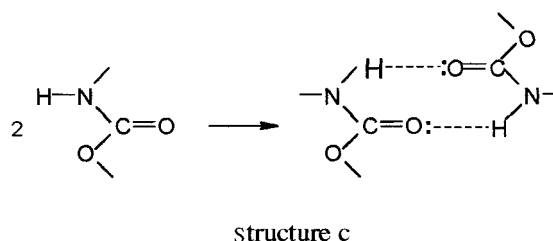
The areas were obtained by integration between $2\theta = 5$ and 35° . The α_x of the studied PUs, with respect to the crystallinity index of type I (α_{xI}) and type II (α_{xII}) crystal forms, are listed in Table IV.

It can be seen that the values of α_x are very small and, within the limit of errors, can be considered equal for all the samples we analyzed. The α_x values for PU-A and PU-B increase with an increasing urethane concentration up to 1.97 mol -NH-COO-/1000 g polymer and then decrease. All the analyzed samples show almost the same behavior for α_{xI} and α_{xII} .

The increase of α_x with increasing urethane concentration up to 2 mol -NH-COO-/1000 g polymer can be correlated with the presence of some ordered mixed structures, which chiefly appear because of the interaction of the hard segments with each other or with the soft segments. Thus, in the case of PU-A and PU-B the electrons of the double bonds from the soft segments form weak hydrogen bonds with urethane (structure a), while -COO- from PU-C are associated with urethane by means of π electrons, which are delocalized from the ester carbonyl (structure b):



Simultaneously, other important reactions between urethane groups takes place, leading to the neutral stiff structure (structure c):



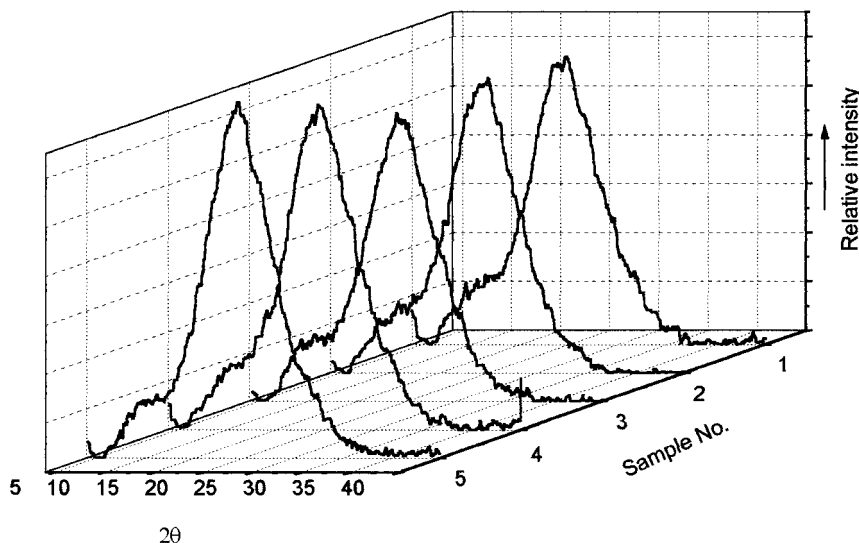
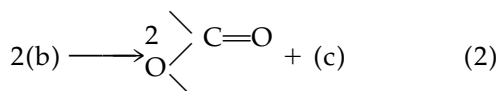
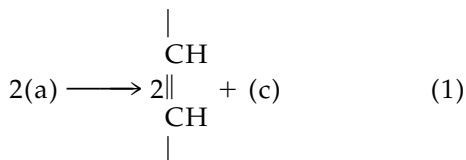


Figure 4 The effect of the urethane concentration on the WAXS intensity of PU-A₁₋₅.

The appearance of the dipoles with structures a and b is supported by the fact that the conductivity of the analyzed PUs increases with the urethane concentration up to 2 mol —NH—COO—/1000 g polymer.¹⁵ Structures a and b prevail up to 2 mol —NH—COO—/1000 g polymer, after which they can react themselves, leading to structure c and the soft segments, as in eqs. (1) and (2):



Equations (1) and (2) show that the soft segment concentration increases the around 2 mol —NH—COO—/1000 g polymer, the phenomenon being translated by a decrease of α_x .

Physicomechanical properties

The variation of the initial modulus versus the urethane concentration is shown in Figure 7.

As can be noted, PU-A and PU-B exhibit a similar dependence of the initial modulus on the urethane concentration. Thus, it increases with the urethane concentration up to a maximum of 1.96 mol —NH—COO—/1000 g polymer, then it decreases in the range of 1.96–2.36 mol —NH—COO—/1000 g polymer and reaches the initial starting values. The dependence of the initial modulus on the urethane concentration for PU-C is completely different than

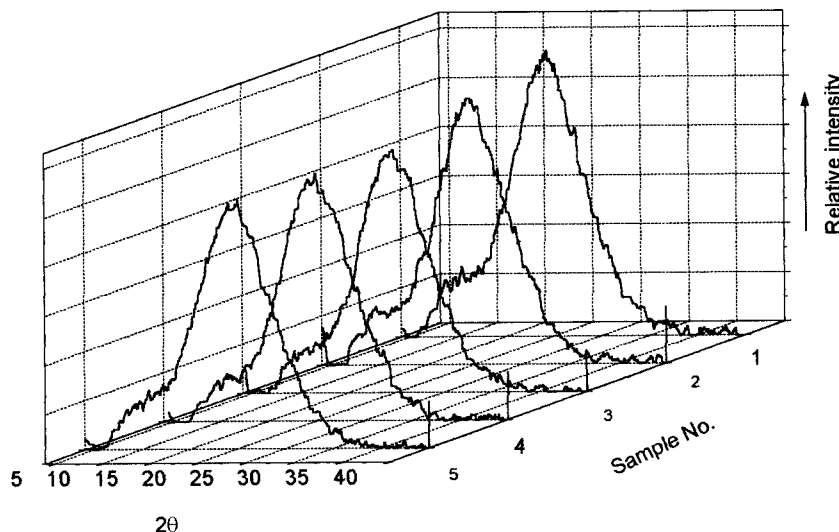


Figure 5 The effect of the urethane concentration on the WAXS intensity of PU-B₁₋₅.

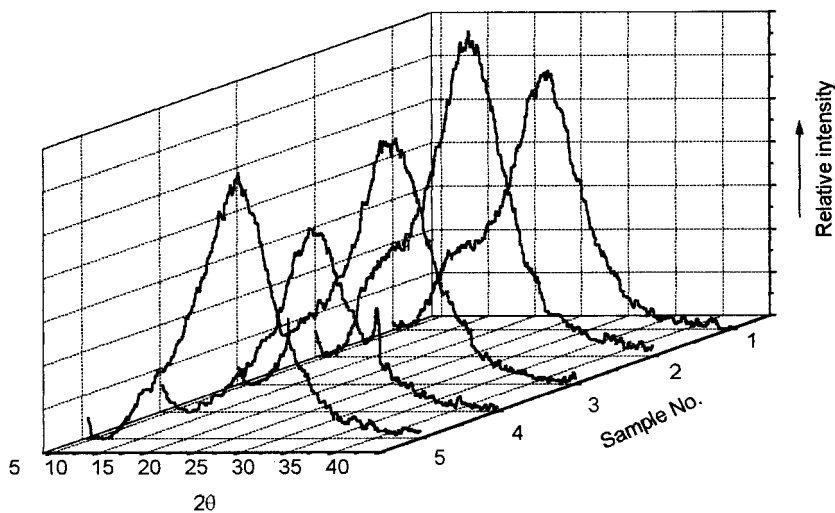


Figure 6 The effect of the urethane concentration on the WAXS intensity of PU-C₁₋₅.

PU-A and PU-B. This time the initial modulus continuously increases up to a maximum value, which corresponds to a 2.36 mol —NH—COO—/1000 g polymer concentration. The values of the initial modulus of both PU-A and PU-B are rather close to each other throughout the concentration range. As compared to PU-A and PU-B, the values determined for the initial modulus of PU-C are higher. The explanation can be found by taking into consideration the intermolecular cohesion due to —CH₂— (0.68 kcal/mol) and —CH=CH— (1.7 kcal/mol) groups in PU-A and PU-B, which are lower versus the —COO— groups (2.9 kcal/mol) from PU-C.⁸ Simultaneously, the soft segments in PU-C are partially bound by hydrogen bonds, which are stronger versus π - π bonds in PU-A and PU-B, respectively.¹⁵

The stress at break values are plotted against the urethane concentration in Figure 8.

For PU-A and PU-B the stress at break increases starting with the initial value measured for 1.72 mol —NH—COO—/1000 g polymer, has a maximum for a urethane concentration of 1.96 mol, then decreases so that for 2.36 mol —NH—COO—/1000 g polymer it has about the same order of magnitude as the starting value. The stress at break for PU-C decreases in the range of 1.72–1.84 mol —NH—COO—/1000 g polymer, then continuously increases with the increasing of the urethane concentration.

Over the entire range of the urethane concentration PU-A and PU-B show close values for the stress at break. PU-C exhibits higher values as against PU-A and PU-B, respectively. Moreover, the dependence of the stress at break on the urethane concentration in both PU-A and PU-B is somewhat analogous to that exhibited by the initial modulus.

TABLE IV
Crystallinity Index (α_x , α_{xI} , and α_{xII}) Determined by WAXS Analysis in Range of Integration $2\theta = 5-35^\circ\text{C}$

Sample	—NH—COO—(mol)/ 1000 g Polymer	ϵT_{am}	ϵT_{cr}	α_x (%)	α_{xI} (%)	α_{xII} (%)
PU-A						
-A ₁	1.72	11,210	250	2.19	0.54	1.65
-A ₂	1.84	11,220	490	4.37	0.69	3.68
-A ₃	1.97	11,190	590	5.27	0.75	4.52
-A ₄	2.08	12,564	500	3.98	0.56	3.42
-A ₅	2.36	13,422	430	3.20	0.45	2.75
PU-B						
-B ₁	1.72	9,559	306	3.10	0.60	2.50
-B ₂	1.84	10,855	298	2.67	0.92	1.75
-B ₃	1.97	11,163	740	6.63	1.38	5.25
-B ₄	2.08	9,735	397	3.92	0.61	3.31
-B ₅	2.36	10,383	307	2.87	0.55	2.32
PU-C						
-C ₁	1.72	12,723	494	3.74	0.63	3.11
-C ₂	1.84	16,424	570	3.36	0.86	2.50
-C ₃	1.97	12,318	544	4.23	0.40	3.83
-C ₄	2.08	8,247	536	6.10	0.63	5.47
-C ₅	2.36	12,144	350	2.80	0.15	2.65

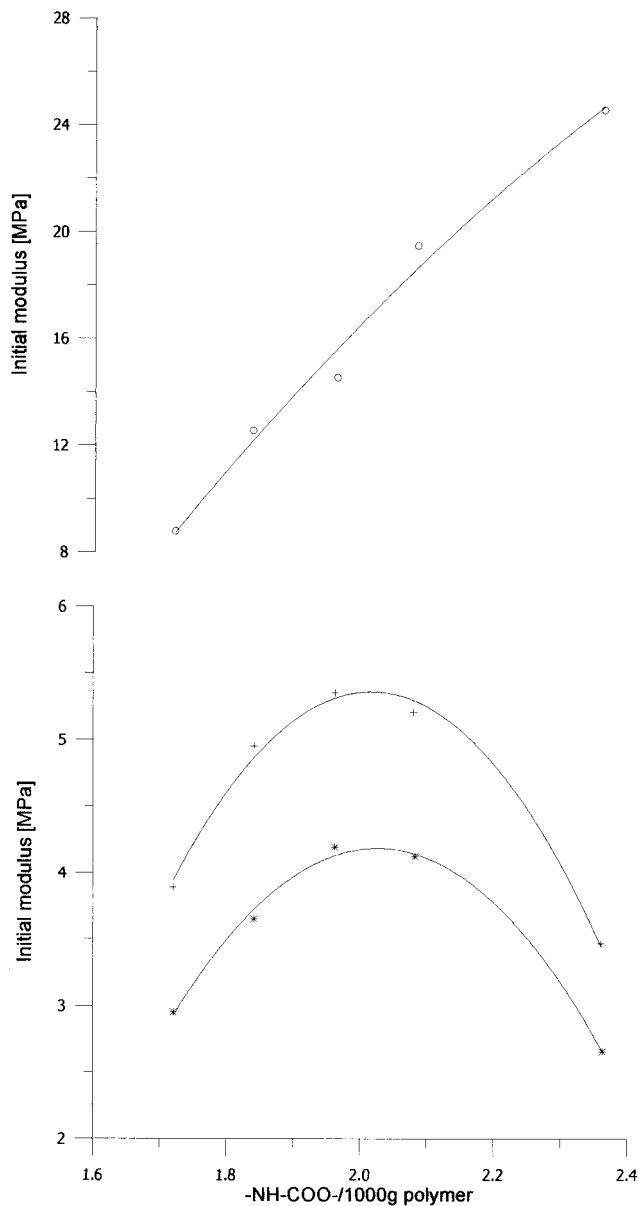


Figure 7 The initial modulus values of PU-A, (+) PU-B, and (○) PU-C versus the concentration of urethane.

Another mechanical property measured in this study was the elongation at break. The dependence of the elongation at break on the urethane concentration for the tested PUs is shown in Figure 9.

As in the case of both the initial modulus and the stress at break, PU-A and PU-B show approximately similar variations of the elongation at break versus the urethane concentration. The elongation at break of PU-A and PU-B decreases starting with the initial value of the urethane concentration (1.72 mol $\text{—NH—COO—/1000 g polymer}$), has a minimum at 1.96 mol urethane concentration, then increases with high values up to 2.08 mol $\text{—NH—COO—/1000 g polymer}$. Beginning with this value the elongation at break slightly increases up to a 2.36 mol urethane

concentration. In the case of PU-C the elongation at break continuously decreases in the interval between 1.72 and 2.36 mol urethane.

The values of the stiffness measured for the three PUs analyzed in this study were obtained by integration of the area under each stress–strain curve. Figure 10 shows plots the stiffness versus the urethane concentration.

For PU-A and PU-B the stiffness increases in the range of 1.72–1.96 mol urethane concentrations, then it continuously decreases. The stiffness of PU-C is increased through the concentration range that is used.

CONCLUSIONS

In the case of PU-C the T_g increases continuously with an increase of the urethane concentration. For PU-A

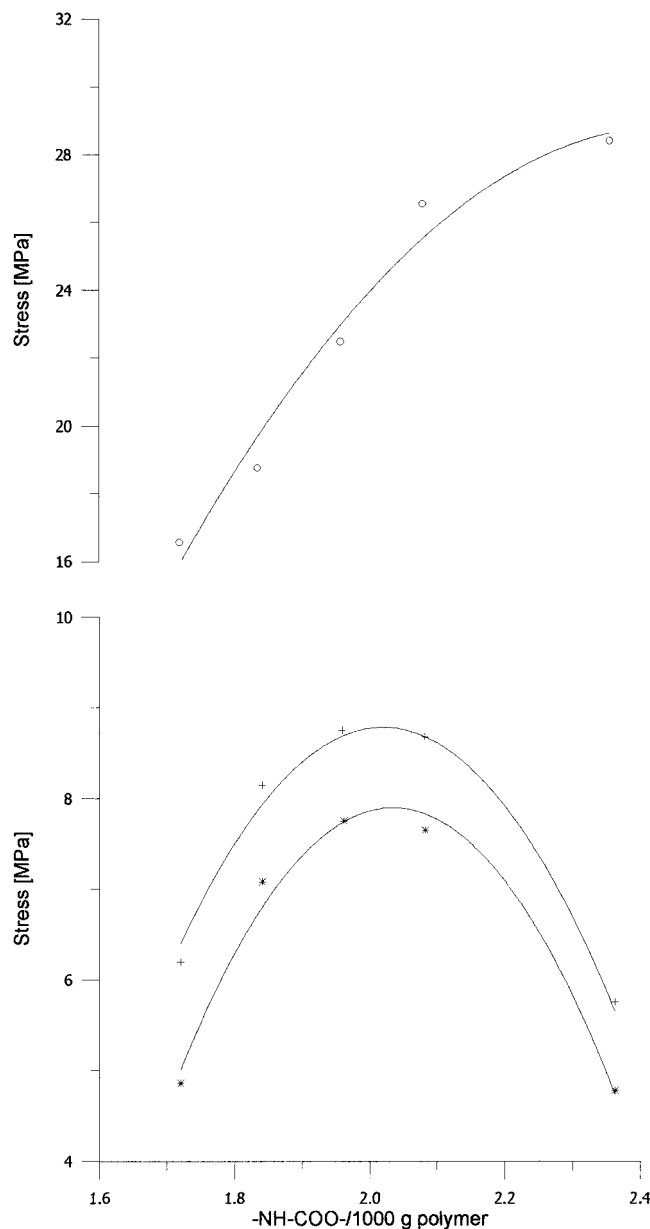


Figure 8 The stress at break values of PU-A, (+) PU-B, and (○) PU-C versus the concentration of urethane.

and PU-B the T_g increases up to 2 mol urethane/1000 g polymer and then a gentle decrease is observed. This behavior indicates a more pronounced phase segregation for PU-A and PU-B than for PU-C.

All the tested PUs show that the α_x value increases up to 2 mol urethane/1000 g polymer and then decreases. This phenomenon shows that, up to 2 mol urethane/1000 g polymer, the urethane groups form preponderant ordered structures with both the double bonds and the esteric groups forming the soft chains of the polymeric matrix. Above a 2 mol —NH—COO— /1000 g polymer concentration the urethane-urethane structures dominate.

The initial modulus of elasticity, as well as the resistance at break, for PU-A and PU-B evolve after a curve as a parabola with a maximum at around 2 mol —NH—COO— /1000 g polymer. For PU-C the two mechanical parameters continuously increase with the increasing of the urethane concentration.

The stress at break for all the PUs under testing decreases with the increase of the urethane concentration up to 2 mol —NH—COO— /1000 g polymer. Above this concentration the stress at break continuously increases in both PU-A and PU-B, but PU-C shows a mild decrease.

These investigations provided evidence that for PUs with lower concentration of urethane the interactions between the hard and soft segments having double bonds and between the hard and the esteric groups from the polymeric chains prevail. The results reported in this study suggest that, when a PU is planned for commercial use, the concentration in the urethane structures must be taken into account, regardless of

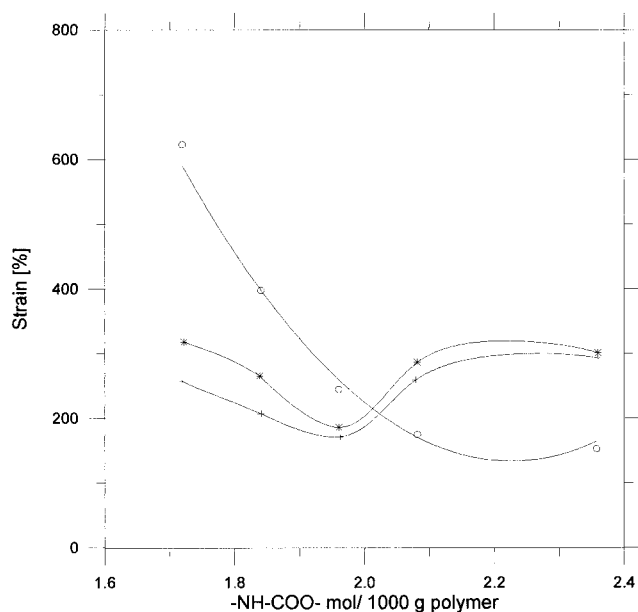


Figure 9 The elongation at break values of PU-A, (+) PU-B, and (O) PU-C versus the concentration of urethane.

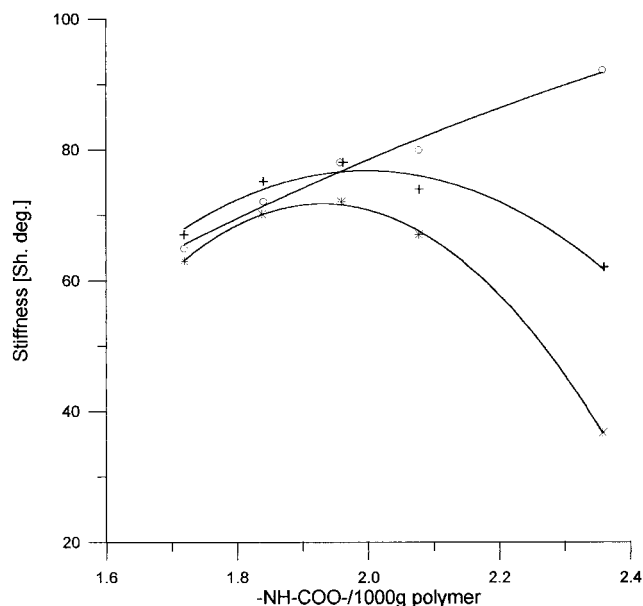


Figure 10 The stiffness values of PU-A, (+) PU-B, and (O) PU-C versus the concentration of urethane.

the nature of the soft macromolecular structures. This concentration is indicated to be higher than 2 mol urethane/1000 g polymer.

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