Segmented polyurethane elastomers by nonisocyanate route

Juliana Nanclares,[1] Zoran S. Petrović,[2] Ivan Javni,[2] Mihail Ionescu,[2] Franklin Jaramillo[1]

[1]Centro de Investigación, Innovación y Desarrollo de Materiales – CIDEMAT, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia
[2]Kansas Polymer Research Center, Pittsburg State University, Pittsburg, Kansas 66762
Correspondence to: F. Jaramillo (E-mail: franklin.jaramillo@udea.edu.co)

ABSTRACT: Novel segmented polyurethane elastomers were successfully synthesized by a nonisocyanate route using dicyclic carbonates as precursors for both soft and hard segments. The hard segment was prepared from the dicyclic carbonate of bisphenol A and *m*-xylylenediamine as chain extender. The soft segment was poly(tetramethylene ether) glycol of molecular weight 1000. Three polyurethanes with different morphologies were made with soft segment concentration of 70, 50, and 30%. Method of synthesis consisted in preparation of dicyclic carbonate of bisphenol A from a commercial epoxy resin and carbon dioxide, while dicyclic carbonate of poly(tetramethylene ether) glycol (PTMEG) was made from previously prepared diglycidyl ether of PTMEG and carbon dioxide. Polymers were prepared by reacting dicyclic carbonates with *m*-xylylenediamine by one-pot process. The monomers and polymers were characterized by Fourier transform infrared spectroscopy, differential scanning chromatography, thermogravimetric analysis, ^{1}H NMR, ^{13}C NMR, scanning electron microscopy, and mechanical measurements. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42492.

INTRODUCTION

Thermoplastic polyurethane (TPU) is the term used in industry to describe a special class of elastomers that can be processed by injection molding and extrusion. These are segmented block copolymers consisting of alternating hard and soft segments. While soft segments are responsible for high elasticity, good elastic recovery, and high elongation at break, hard segments act as physical cross-links that prevent plastic deformation under mechanical stress. Due to incompatibility of soft and hard phases, they form a two-phase structure characterized by domains whose concentration, size, and shape define mechanical properties. Hard domains (HD) melt at high temperature allowing flow necessary for processing but they are reformed upon cooling to act as physical cross-links and also fillers. Typically segmented polyurethanes are prepared from a macro diol (polyether or polyester of molecular weight between around 650 and 2000), a diisocyanate, and a short diol (chain extender), which with diisocyanate forms hard segments. Depending on the soft segment concentration (SSC), morphology of these polyurethanes varies from disperse hard domains suspended in the soft matrix at high SSC, to co-continuous phases at about equal soft and hard phase content, to soft phase dispersed in the hard phase matrix at low SSC.[1,2]

TPUs exhibit excellent thermal and mechanical properties, but there are some problems concerning the synthesis and application of polyurethanes. The first disadvantage associated with the conventional synthesis of TPU is the toxicity of diisocyanates. This reagent is generally very harmful for human health, particularly for people exposed during polyurethanes synthesis and could entail adverse health effects such as asthma, dermatitis, conjunctivitis, and acute poisoning.[3] To avoid issues with isocyanates, extensive efforts are made to find alternative routes for making nonisocyanate polyurethanes (NIPU) mostly for coatings and adhesives.[3–6]

Urethane can be obtained without isocyanate from five-membered cyclic carbonate and amine as shown in Figure 1.

Polyurethanes synthesized using this strategy contain, additionally, hydroxyl group on the *β*-carbon atom of the urethane, giving the product a greater degree of inter- and intramolecular hydrogen bonding, which are expected to impart higher chemical and hydrolysis resistance. Due to the fact that by this methodology biurets and allophanates are not formed, the NIPUs are expected to be more thermally stable than the similar TPUs obtained from isocyanates.[3] Also, the hydroxyl group increases hydrophilicity and water absorption of polyurethane, and may be favorable for biomedical and other applications where these properties are desirable.

The synthesis, characterization, and properties of NIPUs have been studied by different authors.[5,7–14] Steblyanko *et al.*[7]
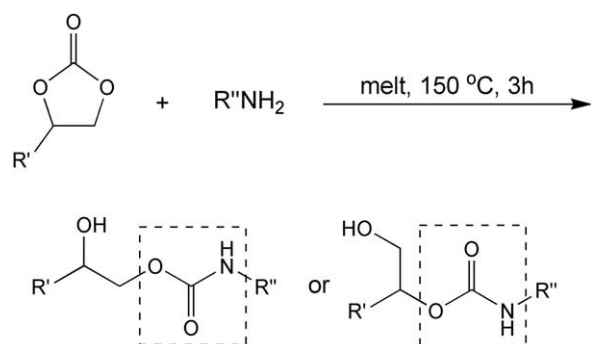
Figure 1. Urethane formation from carbonate and amine.

synthesized a bifunctional five-membered dicyclic carbonate from carbon dioxide and diglycidyl terephthalate, and then these monomers were employed to obtain NIPUs with diamines. The reaction was carried out in DMF at room temperature to give the corresponding polyhydroxyurethane with M_n in the range of 6300–13,200 in good yields. Mi-Ra Kim[11] studied the influence of structure of the diamines on polyhydroxyurethane properties. The polymers were synthesized by polyaddition of a bicyclic carbonate, and both aromatic and aliphatic amines. They found that the polyhydroxyurethane synthesized from aromatic diamines showed higher thermal stability than those from aliphatic amines because of the stiffness of the aromatic chain. This work shows that aromatic diamines yielded lower molecular weight polymers compared to that from aliphatic amine. Renewable-based NIPU have been synthesized by Javni et al.[9] First, they obtained carbonated soybean oil (CSBO) from epoxidized soybean oil (ESBO) in a high yield and low level of residual epoxy in CSBO using a 3.4 g catalyst/100 g ESBO, at 140°C and 1.03 MPa of CO_2. They found that the stoichiometric carbonate-to-amine ratio in the reaction between CSBO and aliphatic amines produced cross-linked polymers of the highest density and the highest glass transition temperature, hardness, and tensile strength. Nonstoichiometric carbonate-to-amine ratios resulted in lower properties. Recently, the synthesis of NIPU from isosorbide dicyclic carbonates and four diamines was reported.[8] These polymers exhibited T_g values in the range from −8 to 59°C, and acceptable thermal stability. Except for a few works,[15] most of this research involved the synthesis of thermoset polyurethanes.

To our knowledge, no thermoplastic polyurethane elastomers were prepared by nonisocyanate route. We are reporting the synthesis and properties of thermoplastic, segmented polyurethanes by a nonisocyanate route. The method used in this work involved preparation of PTMEG dicyclic carbonates, as precursors for soft segments, and preparation of diglycidyl ether of bisphenol A (DGEBA) dicyclic carbonate, which when reacted with m-xylylenediamine (mXDA) gives hard segments. mXDA serves as chain extender to obtain the NIPUs. Dicyclic carbonates of bisphenol A were synthesized earlier,[6,16] but were not used in segmented polyurethanes. Dicyclic carbonates were prepared from corresponding epoxides (diglycidyl ethers) and carbon dioxide. While DGEBA is a commercial product, diglycidyl ether of PTMEG required a special preparation. Dicyclic carbonate of PTMEG, as shown in this work, was synthesized

for the first time. PTMEG is one of the typical industrial polyols for the synthesis of TPU by conventional methods imparting excellent properties.[17–21]

In this work, we have synthesized segmented polyurethanes at three soft segment concentrations—70, 50, and 30% SSC—expecting different morphologies and varying properties from a soft elastomer (70% SSC), to hard elastomer (50% SSC) and eventually toughened plastics at 30% SSC. There are a number of references on linear polyurethanes, which technically are thermoplastic urethanes but they would not qualify as TPU as defined above. For example, thermoplastic urethanes by nonisocyanate route synthesized from two monomers from castor oil were single-phase, nonsegmented polymers that could not serve as elastomers.[15] A number of polyurethanes of this type were prepared by nonisocyanate route,[22,23] but they do not belong to the group of thermoplastic elastomers.

EXPERIMENTAL

Materials
Diglycidylether of bisphenol A (DGEBA), poly(tetramethylene ether) glycol (PTMEG), boron trifluoride diethyl etherate(-$C_2H_5)_2O·BF_3$, sodium hydroxide, tin chloride ($SnCl_4$), m-xylylenediamine, and deuterated solvents ($CDCl_3$ and DMSO-d_6) were purchased from Sigma Aldrich and used as received. PTMEG diol had hydroxyl number of 113 mg KOH/g and molecular weight of 1000. DGEBA epoxy oxygen content (EOC) was 9.3% (equivalent weight = 172 g/mol). Tetrabutyl ammonium bromide 99+%(TBAB), dimethylformamide(DMF) 99.8% dry over molecular sieves, and epichlorohydrin 99% were purchased from Fisher Scientific and used as received.

Characterization Methods
Hydroxyl numbers were determined using both phthalic anhydride method and TSI method according to IUPAC 2.241 and ASTM E 1899-97, respectively. The content of oxirane oxygen (%EOC) was obtained using the American Chemical Service Standard: ACS PER-OXI.

A Bruker DPX-300 spectrometer (Billerica, MA) was used to acquire the proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra. Deuterated solvents ($CDCl_3$ and DMSO-d6) and tetramethyl silane (TMS) as internal reference were used. The experiments were carried out at 300 MHz and 16 scans for proton NMR, and at 75 MHz and 1000 scans for carbon NMR, at room temperature.

The FTIR spectra were recorded from 500 to 4000 cm^{-1} on a Shimadzu IRAFFINITY-1 (Japan) using a KBr crystal plate (IR grade). For each sample, a total of 16 scans were collected at 4 cm^{-1} resolution.

Thermogravimetric analysis (TGA) was carried out on a TGA Q50 from TA instruments (New Castle, DE, USA), under nitrogen at a heating rate of 10°C/min from room temperature to 900°C. Differential scanning calorimetry (DSC) analyses were performed under inert atmosphere using TA Instruments (New Castle, DE, USA) DSC Q100, calibrated with indium standard. The sample mass was 10–20 mg. The thermal cycle consisted of heating from room temperature to 200°C, cooling to −90°C,
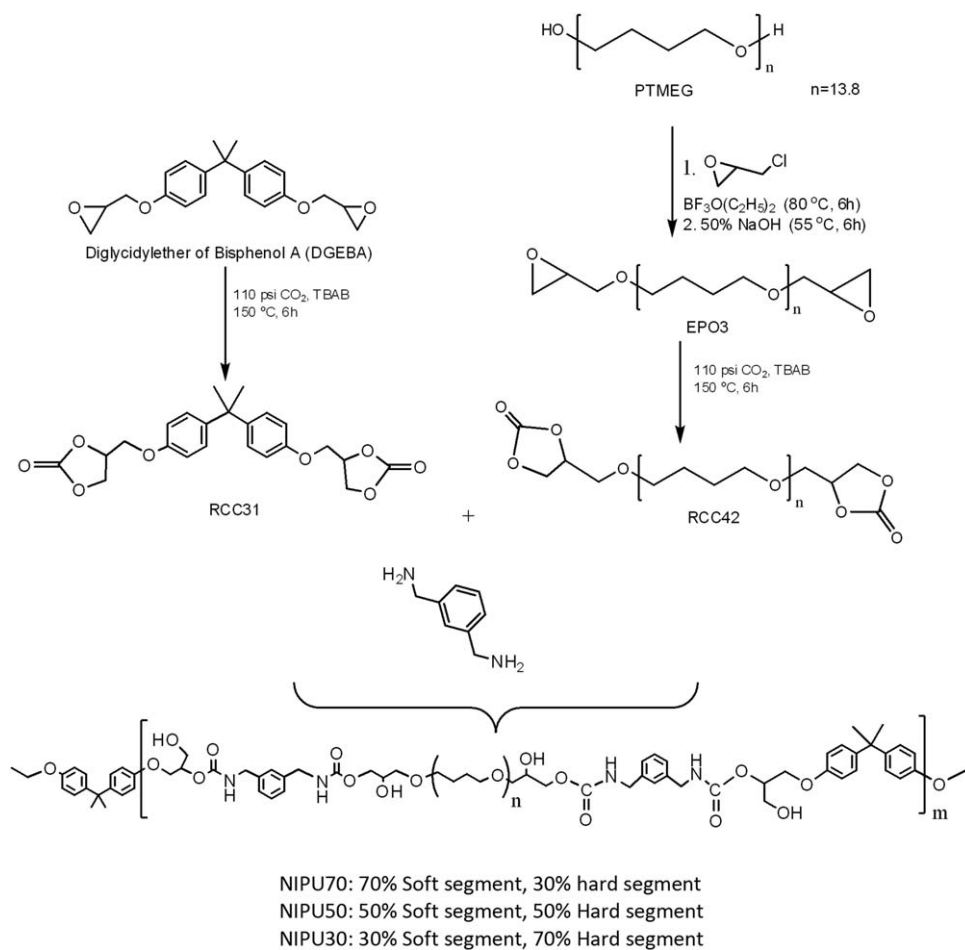
Figure 2. General synthetic strategies for the synthesis of polyurethanes.

and heating again to 200°C. The glass transition temperature (T_g) was determined from the second cycle.

Tensile strength and elongation of NIPUs were determined on QTest II tensile tester (MTS Systems Corp; Eden Prairie, MN, USA) using 30-mm-long samples at room temperature and extension rate of 50 mm/min. Shore hardness was measured by Shore A and D durometers (Pacific Transducer Corp; Los Angeles, CA, USA).

Morphological studies were performed using scanning electron microscopy (SEM) JEOL JSM 6490 LV. Images were taken of the surface made by fracturing the specimen in liquid nitrogen.

Synthesis Methods

Synthesis of Dicyclic Carbonate of DGEBA—RCC31[6]. All the reactions were carried out under nitrogen atmosphere and dry conditions. The synthesis of dicyclic carbonate RCC31 from diglycidyl ether of bisphenol A (DGEBA) and CO_2 was carried out in a closed reactor under pressure. DGEBA (102.01 g, 0.3 mmol) and TBAB (0.52 g, 0.0016 mmol) were charged into the reactor without a solvent. The reactor was mechanically stirred (1200 rpm). The system was purged several times with CO_2 and then pressurized with CO_2 to 0.758 MPa (110 psi). The mixture was stirred for 6 h at 150°C. No further purification was necessary to obtain the final product. The pure product was a white

solid with 97% of yield. ^{1}H NMR (300 MHz, DMSO): δ 6.99 (dd, $J = 80.1$, 8.7 Hz, 4H), 5.13 (m, 1H), 4.62 (t, $J = 8.5$ Hz, 1H), 4.38 (dd, $J = 8.4$, 6.0 Hz, 1H), 4.20 (ddd, $J = 15.8$, 11.3, 3.6 Hz, 2H), 1.58 (s, 3H).^{13}C NMR (75 MHz, DMSO) δ 156.17, 155.34, 143.76, 127.99, 114.47, 75.28, 67.84, 66.48, 41.70, 31.12. Mp: 160°C. s: DMF, DMSO, DMAc, and NMP. ins: THF, acetone, and chloroform.

Synthesis of Diglycidylether of PTMEG (EPO3). The synthesis of diglycidyl ether of PTMEG (designated as EPO3) was carried out successfully using $(C_2H_5)_2O\cdot BF_3$ as a catalyst according to a modified published procedure.[24] The synthesis of EPO3 was performed by reacting PTMEG with epichlorohydrin in the presence of boron trifluoride diethyl etherate catalyst. A glass reactor equipped with stirrer, reflux condenser, and thermometer was charged with PTMEG polyol (100 g, 0.1 mol) and catalyst (0.57 g, 0.004 mol), and the mixture was heated to 80°C. Then with efficient stirring, epichlorohydrin (27.76 g, 0.3 mol) was added over 1 h. The mixture was stirred for 6 h at 80°C. The system was cooled to 55°C and 50% aqueous solution of sodium hydroxide (8.00 g, 2.0 mol) was added dropwise with efficient stirring over 30 min. After stirring for 6 h at 55°C and cooling to room temperature, the suspension was filtered and the filtrate was washed with ethyl acetate. Two phases were separated, and the aqueous phase was extracted with 2 × 100 mL
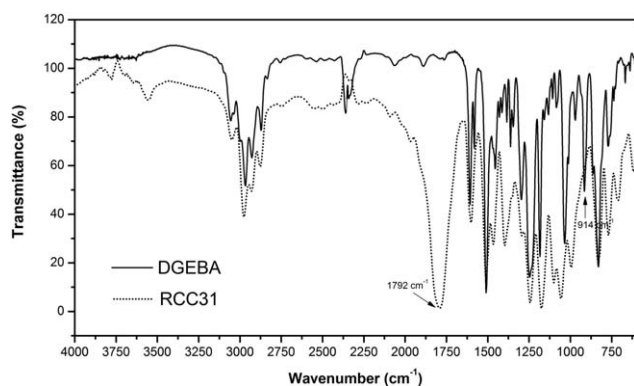
Figure 3. Overlay of DGEBA and RCC31 FTIR spectra.

Figure 5. ^{13}C-NMR of RCC31.

of ethyl acetate. The combined organic phases were dried over magnesium sulfate and filtered. The filtrate was freed from solvent on a rotary evaporator under vacuum. ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.76–3.20 (m), 3.20–3.01 (m), 2.83–2.47 (m), 2.02 (s), 1.57 (d, $J = 3.7$ Hz).

Synthesis of PTMEG Dicyclic Carbonate—RCC42[6]. The synthesis of dicyclic carbonate from diglycidyl ether of PTMEG (EPO3) and CO$_2$ was carried out in a typical procedure. EPO3 (30 g, 27 mmol) and TBAB (0.08 g, 0.46 mmol) were charged into the reactor. No solvent was used. The system was purged several times with CO$_2$, and then the reactor was pressurized with CO$_2$ to a preset pressure of 0.758 MPa. The mixture was mechanically stirred for 6 h at 110°C. Afterward, the reactor was cooled to room temperature and depressurized. No further purification was necessary to obtain the final product. The pure product was obtained with quantitative yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.72 (m, 2H), 4.48–4.23 (dt, 4H), 3.67–3.38 (m, 25H), 3.32 (s, 48H), 1.52 (s, 59H).

Synthesis of Polyurethane NIPU50. The polyurethanes were synthesized by one-pot polymerization process. A typical reaction is as follows: RCC31 (33.6 g, 0.08 mol), RCC42 (50.0 g, 0.04 mol), and diamine (16.35 g, 0.12 mol) were charged into a three-neck round-bottom flask reactor. The mixture was mechanically stirred, and the system was purged several times with N$_2$. The mixture was stirred for around 3 h at 150°C. Segmented polyurethanes of 70% (NIPU70), 50% (NIPU50), and
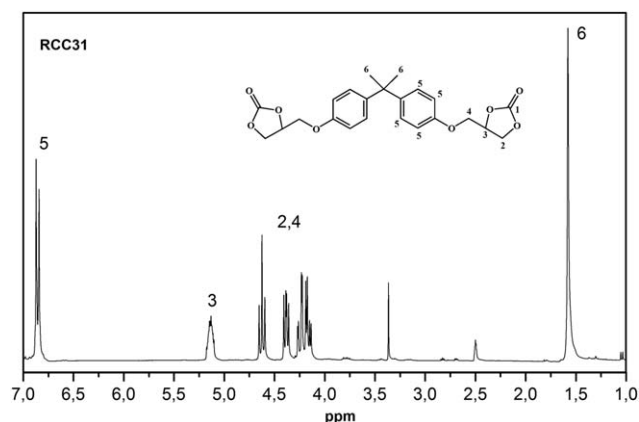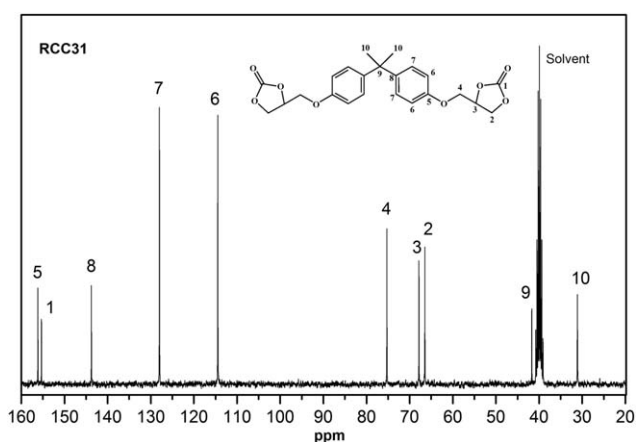
30% (NIPU30) were prepared by this procedure. ^{1}H NMR (300 MHz, DMSO) δ 7.69 (s), 7.31–6.79 (dd), 4.14–3.88 (m), 1.54–1.47(d).

Synthesis of Polyurethane TPU30. This polyurethane was synthesized by one-pot two-step polymerization process. A typical reaction is as follows: calculated amount of PTMEG (dried in a vacuum at 100°C for 1 h) was weighed in a dry three-neck round-bottom flask under dry nitrogen atmosphere and stirred at 60°C. MDI (12.1 g, 0.05 mol) premixed in DMF (*N,N*-dimethylformamide) was added dropwise. After complete addition of MDI, the mixture was stirred for additional 2 h at 60°C to prepare the prepolymer. 1,4-butanediol (3.0 g, 0.03 mol) was added to the prepolymer and further stirred at 60°C for a period of 48 h to prepare the final TPU. The mixture was purified by precipitating in water followed by repeated washings. The precipitate was then dried in vacuum. ^{1}H NMR (300 MHz, DMSO) δ 9.48 (s, 6H), 7.19 (dd, $J = 74.7$, 7.4 Hz, 27H), 4.17–3.91 (m, 12H), 3.76 (s, 4H), 3.50 (s, 31H), 3.29 (s, 22H), 1.67 (s, 13H), 1.46 (s, 24H).

RESULTS AND DISCUSSION

The polyurethane synthesis by nonisocyanate route began with the conversion of diglycidyl ether bisphenol A (DGEBA) into dicyclic
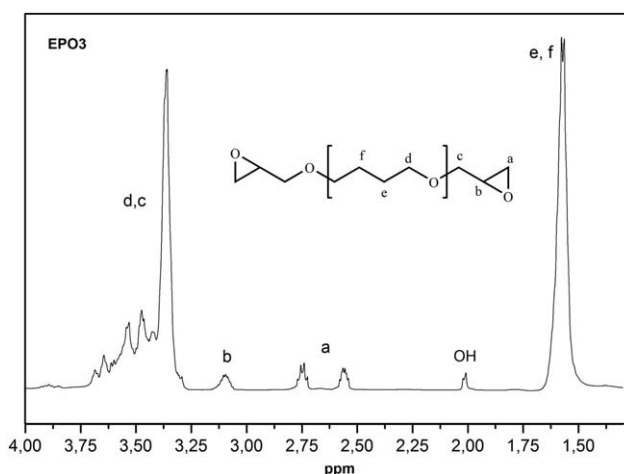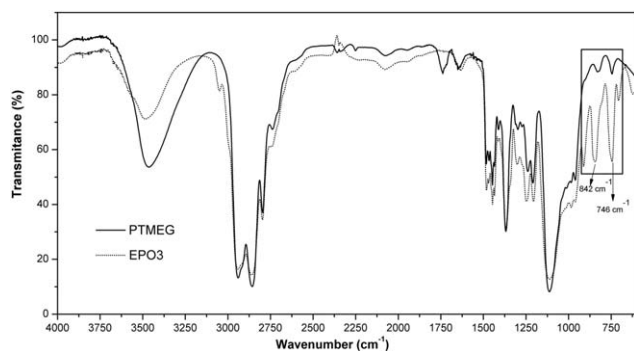

Figure 4. ^{1}H-NMR of RCC31.

Figure 6. ^{1}H-NMR of EPO3.

Figure 7. Overlay of PTMEG and EPO3 FTIR spectra.

Figure 9. FTIR of RCC42 and EPO3.

carbonate RCC31 using high CO_2 pressure and TBAB as a catalyst.[6] Soft segment precursor was prepared by converting PTMEG diol to diglycidyl ether of PTMEG using $(C_2H_5)_2O \cdot BF_3$ as a catalyst. It was then converted to dicyclic carbonate RCC42, using the same methodology as explained above for the RCC31. Finally, the corresponding NIPUs were synthesized by reacting dicyclic carbonate (RCC31 and RCC42) with *m*-xylylenediamine. Figure 2 illustrates the synthetic pathway. The polymers obtained in this work are alternating block copolymers of PTMEG soft segments and DGEBA/*m*XDA hard segments. *m*XDA may react with PTMEG dicyclic carbonate to form longer soft segment with some amine units inside. The reaction between dicyclic carbonates with amines results in the formation of two isomers of polyhydroxyurethanes, each containing a urethane and a hydroxyl group wherein one is secondary, while the other is primary. Figure 2 shows an idealized polymer structure. Thermal and structural properties of the synthesized NIPUs were assessed by means of FTIR, NMR, TGA, and DSC.

Spectroscopic Analysis of Dicyclic Carbonate RCC31 Formation

The conversion of an epoxy group to cyclic carbonate was followed by FTIR. Figure 3 shows the spectrum of DGEBA and RCC31. Strong absorption bands of the DGEBA are peaks at 1610 and 1506 cm^{-1} assigned to the benzene ring stretching, and the asymmetric and symmetric bending peaks of CH_3 at 1459 and 1362 cm^{-1}, respectively.

The new band at 1792 cm^{-1}, associated with the cyclic carbonate and assigned to C=O stretching, confirms the formation of

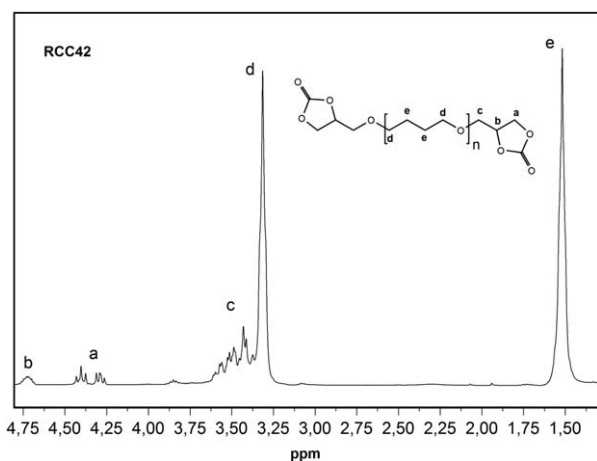cyclic carbonate. Therefore, the peak at about 914 cm^{-1}, which has been assigned to C—C vibrations from the epoxy ring of DGEBA, disappeared completely.

The formation of cyclic carbonate was also confirmed by NMR. Figures 4 and 5 show the ^{1}H-NMR and ^{13}C NMR spectra of RCC31, respectively. It was observed that the typical signals at 3.29, 2.82, and 2.68 ppm of epoxy group in the DGEBA ^{1}H-NMR spectrum disappeared in the final product. New signals associated with the cyclic carbonate appeared at 5.12, 4.62, 4.40, and 4.20 ppm[11] (Figure 4). Furthermore, the signals at 50.20 and 44.26 ppm corresponding to carbons of the epoxy group[11] disappeared completely from the ^{13}C NMR spectrum of RCC31. The peak at 155.34 ppm attributed to the carbonyl of cyclic carbonate confirms the complete conversion of epoxy group (Figure 5).

Properties of Diglycidyl Ether EPO3

The synthesis of diglycidyl ether obtained from PTMEG was successful using $(C_2H_5)_2O \cdot BF_3$ as a catalyst. The content of oxirane oxygen (% EOC) of the product was 2.7%. The value was close to the theoretical of 2.8% EOC for epoxy-terminated PTMEG. The resulting OH number 13.2 mg KOH/g was higher than expected from EOC results, due to interference of epoxy and acid groups in the product.

The presence of the characteristic signals of epoxy group at 3.36 (C$\underline{H}_2$—O—Ar), 3.10 (—C$\underline{H}$ epoxy ring), and 2.64 ppm (—C$\underline{H}_2$ epoxy ring)[25] confirmed the formation of epoxy group by ^{1}H-NMR (Figure 6). Also, the new peaks at 746 and 842 cm^{-1}
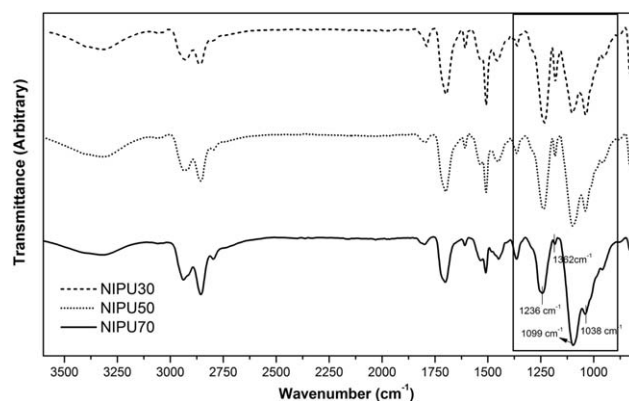

Figure 8. ^{1}H-NMR of RCC42.

Figure 10. FTIR for the series of NIPUs.

Table I. Assignment of Key Peaks in FTIR Spectra for NIPUs

Wavenumber (cm^{-1})	Assignment
3400	O—H stretching
3315	N—H stretching
2929	CH$_2$ asymmetric stretch vibration
2856	CH$_2$ symmetric stretch vibration
1800	C=O stretching of cyclic carbonate
1697	H-bonded carbonyl in urethane
1610	C—C aromatic stretch vibration
1537	C—N+ N—H (amide II) stretching
1508	C—C aromatic stretch vibration
1452	CH$_3$ asymmetric deformation
1363	C—N stretching
1236	Asymmetric stretch N—CO—O+ stretching C—O—C
1180	CH aromatic in-plane deformation
1099	Stretching vibration of the C-O ether
1038	C—N vibration
956	Bending vibration of C—H
827	CH aromatic out of plane deformation

characteristic of epoxy ring mode corresponding to C—C and C—O stretching of ester were observed by FTIR (Figure 7).

Spectroscopic Analysis of Dicyclic Carbonate RCC42 Formation

This compound was synthesized according to the same procedure used for RCC31, using EPO3 as a raw material, at 150°C and with a high pressure of CO$_2$. Total conversion was confirmed by total disappearance of the protons of the epoxy group between 3.10 and 2.64 ppm and also by the appearance of signals corresponding to the carbonate protons between 4.70 and 4.26 ppm in the ^{1}H-NMR (Figure 8). Additionally, the new band at 1800 cm^{-1}, associated with the cyclic carbonate forma-

tion and assigned to stretching of C=O bond, was observed in the FTIR spectrum (Figure 9). The loss of epoxy ring bands at 843 and 746 cm^{-1} indicates the consumption of epoxy groups.

Analysis of Polyurethanes NIPU70-30 and TPU30

TPUs were synthesized using a dicyclic carbonate (RCC31 and RCC42)–amine reaction. The reaction between RCC31 and *m*-xylylenediamine formed the hard segment of the polymer and the soft segment was formed with the reaction between RCC42 and *m*-xylylenediamine.

The polyurethanes were insoluble in common organic solvents due to hydrogen bonding of hydroxyl and urethane groups (THF, methanol, acetone, and water), and were swollen only in aprotic solvents, such as *N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), after 24 h. Possibility of slight cross-linking due to unspecified side reactions is not completely excluded.

The polymers synthesized in this work exhibited typical infrared characteristics of polyurethanes (Figure 10). The peaks at 3400 and 3315 cm^{-1} were assigned to H-bonded O—H stretching and N—H stretching, respectively. Mishra et al.[26] reported three kinds of N—H stretching in segmented polyurethanes: at 3499, 3372, and 3306 cm^{-1}, assigned to free N—H groups, N—H groups bonded with carbonyl (in hard segments: type I, N—H···O=C) and ether oxygen (in polyether soft segments: type II, N—H···C—O—C). All NIPUs prepared in this work exhibited a peak around 3320 cm^{-1}, suggesting that N—H groups are involved in hydrogen bonding type II. The FTIR spectra showed the presence of unreacted cyclic carbonate (RCC31 and RCC42) monomers due to a low-intensity peak at 1800 cm^{-1}. The position of the carbonyl absorption bands depends on the overall structure and temperature, but generally H-bonded carbonyl in polyurethanes appears at 1700–1720 cm^{-1}, whereas free (non-hydrogen-bonded) one appears at 1730–1740 cm^{-1}.[27] All infrared spectra show only hydrogen-bonded carbonyls at around 1700 cm^{-1}. The band at 1537 cm^{-1} is characteristic of C—N + N—H bonds. The absorption band at about 1236 cm^{-1} is assigned to the asymmetric
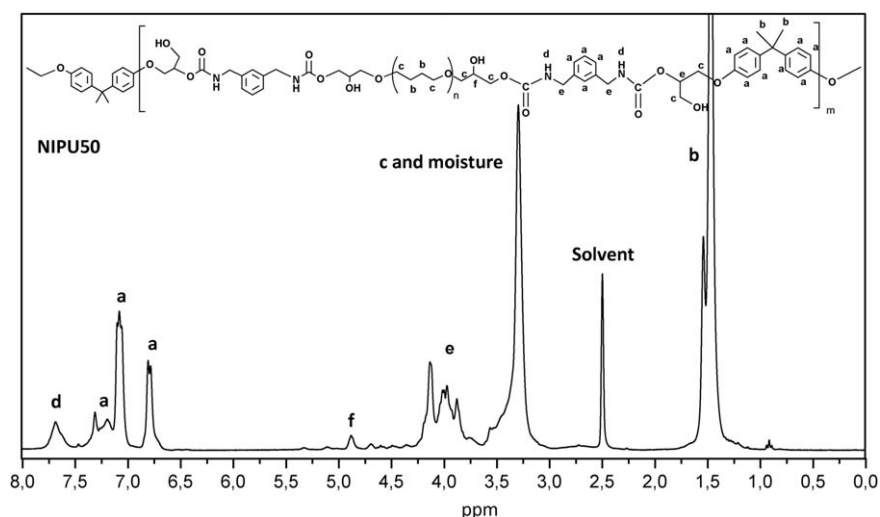
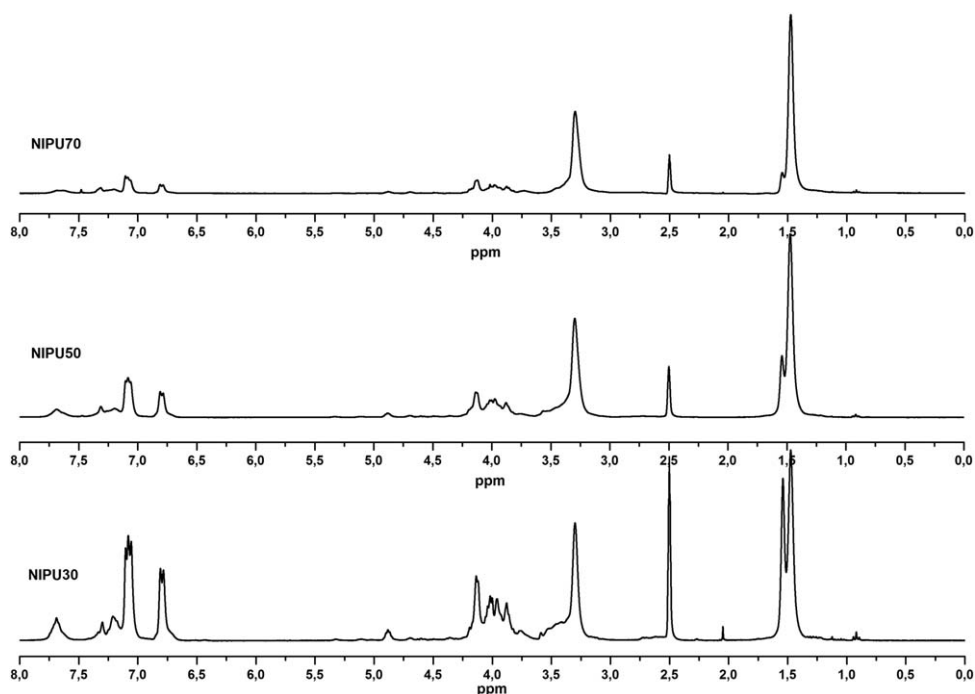**Figure 11.** ^{1}H-NMR spectrum of NIPU50.

Figure 12. ^{1}H-NMR spectrum of NIPUs.

stretch N—CO—O and stretching C—O—C of urethane group. It was found that this peak increased with the increase of the hard segment content. The corresponding aromatic peaks of cyclocarbonate and xylylene appeared at 1180 and 827 cm^{-1}, increasing with the increasing of hard segment content. The key peaks assignments are reported in Table I.

The key difference between FTIR NIPUs spectra is the intensity ratio of peaks at 1236, 1099, and 1038 cm^{-1}, assigned to N—CO—O + C—O—C ester, C—O vibration of ether bond, and C—N vibration, respectively. NIPU30 presented the highest intensity of the band at 1236 cm^{-1} due to higher content of N—CO—O + C—O—C from the hard segment. This can be the result of an increased hydrogen bonding between the C—O of ether and N—H (HS–SS interaction).

The chemical structures of the polymers were confirmed using ^{1}H NMR. Figure 11 shows the ^{1}H NMR spectrum for a typical NIPU50, and Figure 12 shows the comparison between the series of NIPUs. The signal of urethane group N—H was observed at 7.69 ppm, and the signals associated with cyclic carbonate group disappeared (5.12, 4.62, 4.40, and 4.20 ppm; Figure 11). The signals at 1.54 and 1.47 ppm were assigned to CH$_3$ protons of RCC31 from hard segments and internal methylene protons (CH$_2$ of RCC42) in the soft segment, respectively. The signals corresponding to aromatic protons of the hard segment appeared in the region between 7.10 and 6.79 ppm. Furthermore, the protons associated to (—OCH$_2$) appeared at 3.30 ppm, and the signals corresponding to (CH$_2$NHCOOCH$_2$) and (OCH$_2$CHOHCH$_2$) were assigned to the peak between 4.13 and 3.83 ppm.

Thermal Properties of NIPU

In two-phase systems like segmented polyurethanes, several transitions are possible, such as, glass transition of the soft and hard segment and melting in crystallizing systems. Glass transi-

tion of the soft segment made from PTMEG is determined by molecular weight of the polyol used. The glass transition (onset temperature) of the soft segments based on PTMEG1000 in polyurethanes from MDI/BDO/PTMEG was reported at −60°C.[28] DSC curves of three NIPU samples and reference TPU30 shown in Figure 13 reveal a distinct soft segment glass transition in all samples in the temperature range −70 to 0°C, and the hard segment T_g was generally above room temperature, indicating clearly the existence of phase separation. However, a broad glass transition in NIPU samples indicates some phase mixing, Table II. T_g values (mid-point) in TPU30 and NIPU70 are within experimental error (around −50°C), although for NIPU30 and NIPU50, a temperature of −40°C was found. No melting was observed, indicating that both soft and hard segments are amorphous. Strong hard segment glass transition at 47°C observed in
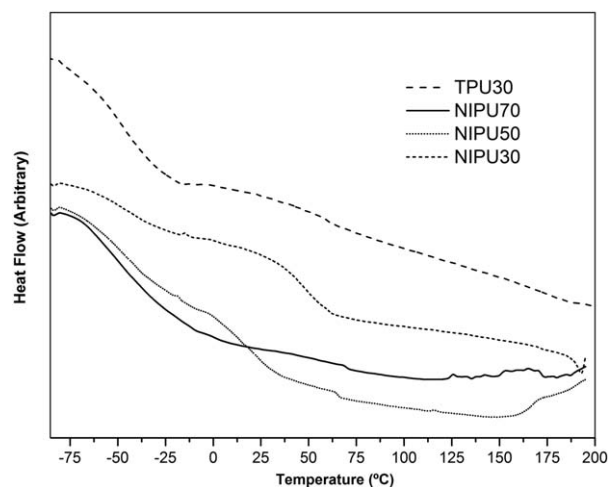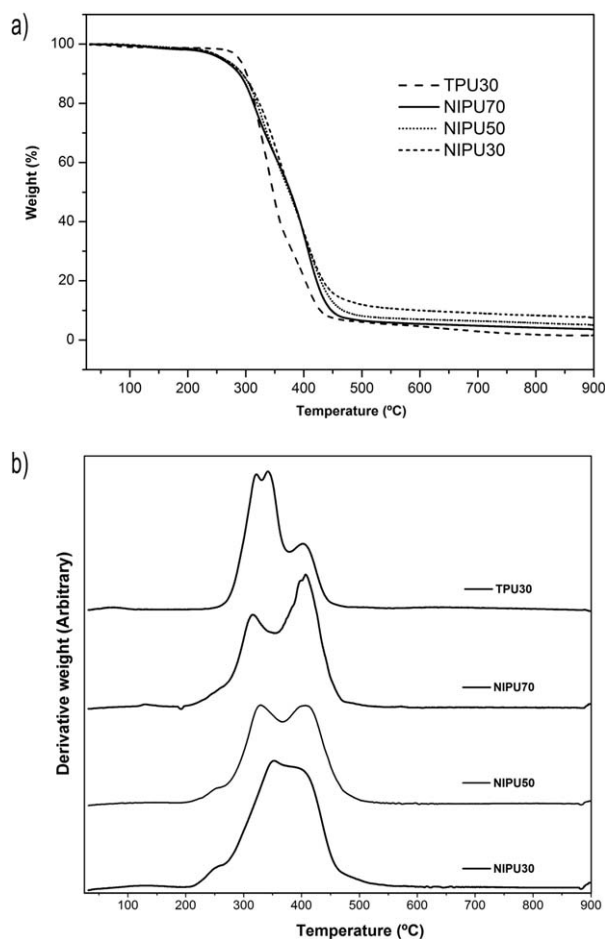

Figure 13. DSC thermograms of NIPUs and TPU.

Table II. Thermal Properties of NIPUs

Sample	SSC (%)	$T_{g(SS)}$ (°C)	$T_{g(HS)}$ (°C)	Residue at 900°C (wt %)	Temperature of 5% weight loss (°C)
TPU30	30	−47	60	1.6	290
NIPU70	70	−49	–	3.5	258
NIPU50	50	−40	14	5.0	263
NIPU30	30	−40	47	7.4	262

NIPU30 shifts to 14°C for NIPU50 and is not discernible for NIPU70. T_g is dependent on molecular weight of hard segments, being 2300 Da for NIPU30, 1000 Da for NIPU50, and 430 Da for NIPU70. The number average molecular weight of hard segments depends on SSC and molecular weight of soft segment, M_{ss}, and can be calculated from the expression[2]: $M_{hs} = (100 − SSC) \times M_{ss}/SSC$. Since repeat unit in the hard segment of NIPU consists of DGEBA carbonate–diamine units of molecular weight 564 Da, it is obvious that formation of hard domains in NIPU70 would be difficult, and essentially we may have a single-phase system due to phase mixing. In such cases, hard segment would not have the role of physical cross-links and the material would show plastic behavior during deformation, as will be seen later.

Thermal degradation of new polyurethanes is illustrated by thermogravimatric (TGA and DTG) curves shown in Figure 14(a,b). The onset of degradation is about the same for all NIPU samples and it is lower than that of TPU30. Degradation of polyurethanes starts by degradation of urethane bonds followed by degradation of the soft segments, and it is almost complete at 500°C.[29] In the case of NIPU, an additional factor may be the effect of hydroxyl groups and their loss by dehydration, but the true degradation mechanism would require a separate study. Initial degradation is faster in NIPU polymers, but the weight loss is lower at later stages as the cross-over occurs at about 20% loss. There is a little difference in the rate of degradation of NIPU samples. Figure 14(b) shows two major peaks on differential thermogravimetric (DTG) curves, where the lower peak is dominated by urethane group degradation and higher peak by soft segment degradation. Thus, these NIPU samples showed lower thermal stability judged by the onset temperature of degradation.

Mechanical Properties

A factor which plays an extremely important role on the mechanical properties is the amount of phase separation, which is also influenced by SSC. Different behaviors could be observed from the stress–strain curves (Figure 15; Table III). NIPU with 70% SSC presented a typical plastic deformation with elongation up to 2480% and low tensile strength at 0.8 MPa, characteristic of a single-phase material. NIPU with the lowest content of soft segment (NIPU30) had the highest tangent modulus of 331 MPa, with tensile strength of 12 MPa, and a brittle fracture at 6% elongation. This NIPU is characterized by a continuous hard phase with dispersed soft segments. NIPU50 is an elastomer with tangent modulus of 5 MPa, elongation break at 650%, and
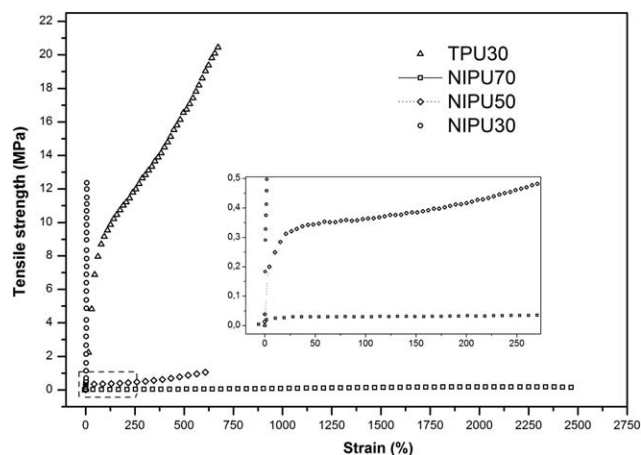

Figure 14. (a) TGA and (b) DTG of NIPUs and TPU30.

Figure 15. Tensile stress–strain curves of NIPUs with 50 and 70% SSC.

Table III. Mechanical Properties and T_g of NIPUs

Polymer	SSC (%)	Shore A hardness	Shore D hardness	Tensile strength (MPa)	Elongation break (%)	Tangent modulus[a] (MPa)
TPU30	30		38	20.42	677	15.66
NIPU70	70	4	–	0.18	2479	0.19
NIPU50	50	–	12	1.11	645	5.01
NIPU30	30	–	77	12.36	6	331.36

[a] Calculated in the Hookean region.

relatively low tensile strength of 1 MPa due to poor phase separation. The difference in the stress–strain behavior between the polyurethane with NIPU30 and TPU30 was dramatic. The former, contrary to the conventional one, is more brittle and shows no apparent yield point, suggesting lower segregation. This behavior clearly illustrates the difference in structure of two polyurethanes
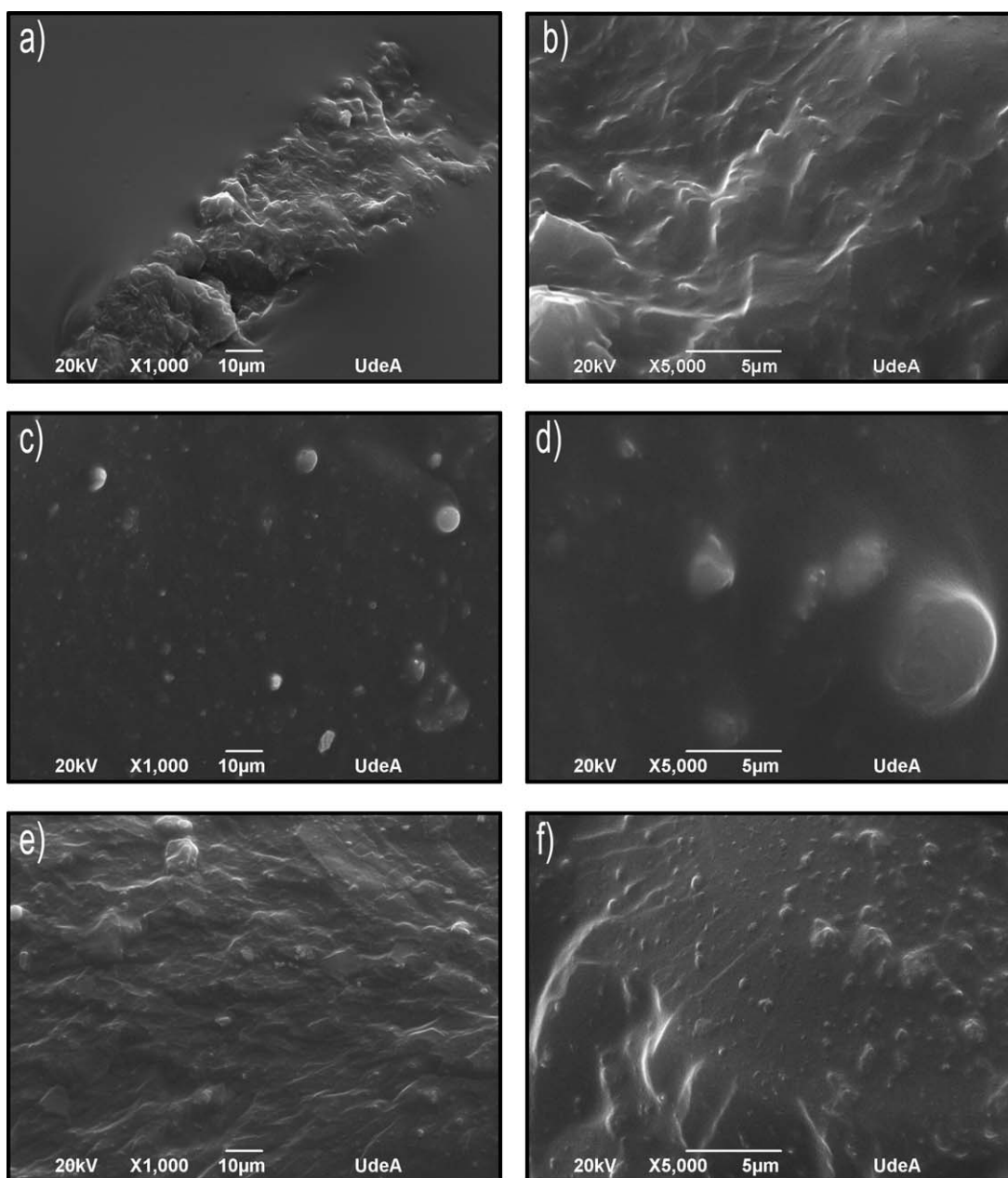

Figure 16. SEM micrographs of NIPUs: (a) NIPU70, (b) NIPU70, (c) NIPU50, (d) NIPU50, (e) NIPU30, and (f) NIPU30.

with the same content of hard and soft segments but prepared from dicyclic carbonate or with diisocyanate. The values for hardness presented in Table III are also consistent with the fragile and elastomeric behavior found by the mechanical properties. NIPU70 presented the lowest hardness and NIPU30 the highest. The effect of hydroxyl groups on mechanical properties is not clear because other structural differences are large. The structure of hard segments in this work is not optimized and was conditioned on availability of raw materials. Bisphenol A has two methyl groups which may prevent packing into crystalline lattice and *m*-xylylenediamine introduces irregularity in the structure. Utilizing diglycidyl ether of diphenyl methane and *p*-xylylene diamine, instead of *m*-XDA, would give a more regular structure, possible crystallization of hard segments, better phase separation, and better properties. Also, a selection of higher molecular weight soft segments would result in higher hard segment molecular weights, better phase separation, and larger domain sizes and thus better properties.

Scanning Electron Microscopy

SEM was carried out to study the effect of SSC on the size and shape of the resulting hard domains. Figure 16 shows the SEM images of the NIPUs.

Fractured surface of NIPU70 is rough but no distinct globules of the hard phase could be observed, which is consistent with the assumed single-phase morphology and plastic deformation in stress–strain tests. NIPU50 displayed micron-size globules which possibly represent association of hard domains. Fine structure of the phases would require more detailed study of morphology and utilization of different techniques such as atomic force microscopy and small angle scattering, which was not available. The surface of NIPU30 was relatively rough as seen in brittle fracture of glassy polymers with some globules of unidentified nature. The dominating component in NIPU30 is hard phase with embedded soft domains but their identification would require separate study. Clear phase separation can be clearly observed only in NIPU50.

CONCLUSIONS

Novel segmented polyurethanes were successfully synthesized by a nonisocyanate route. The polymers were prepared from the diglycidyl ether of bisphenol A, carbon dioxide, *m*-xylylenediamine, and epoxidized PTMEG. Polymers were insoluble in standard solvents for polyurethanes. The polymer with 30% soft segment was a hard plastic while those with 50 and 70% SSC were elastomers. Due to lower reactivity of components compared with isocyanate chemistry, the polymers were assumed to have lower molecular weights compared to equivalent isocyanate-based products, which may have affected their properties. Although the structure of polyurethanes was not optimized, we have demonstrated the feasibility of making viable nonisocyanate segmented polyurethane elastomers. Improvement in structure and properties could be achieved with a more careful selection of diglycidyl ethers and linear diamines.

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