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Syntheses and characterization of novel biostable polyisobutylene based thermoplastic polyurethanes

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ABSTRACT

The synthesis of polyisobutylene (PIB) based thermoplastic polyurethanes (TPU) with enhanced mechanical properties have been accomplished using poly(tetramethylene oxide) (PTMO) as a compatibilizer. PIB TPUs with Shore 60–100 A hardness were prepared by employing PIB diols (hydroxyallyl telechelic PIBs) for the soft segment and 4,4′-methylenebis(phenylisocyanate) (MDI) and 1,4-butanediol (BDO) for the hard segment. The TPUs exhibited number average molecular weight (M_n) in the range of 83,000–110,000 g/mol with polydispersity indices (PDIs) = 1.8–3.1. These TPUs, however, were inferior compared to commercial TPUs such as Pellethane™ (Dow Chemical Co.) as they exhibited low tensile strength (6–15 MPa) and/or ultimate elongation (30–400%). Processing of the harder compositions was also difficult and some could not be compression molded into flat sheets for testing. Differential Scanning Calorimetry (DSC) showed the presence of high melting ($\geq$200 °C) crystalline hard segments suggesting longer – MDI–BDO – sequences than expected based on the stoichiometry. Easily processable TPUs with excellent mechanical properties (tensile strength up to 40 MPa, ultimate elongation up to 740%) were obtained by incorporating PTMO in the soft segment. Examination of PIB–PTMO TPUs with varying hard: soft compositions (20:80, 35:65 and 40:60 wt:wt) and Shore hardness (60 A, 80 A and 95 A) indicated that substituting 10–30 wt% of PIB diol with PTMO diol is sufficient to reach mechanical properties similar to Pellethanes.

1. Introduction

Segmented thermoplastic polyurethane (TPU) elastomers are of immense importance owing to their use as various biomaterials [1]. Polyurethanes offer a broad range of physical properties and characteristics, including high tensile and tear strength, chemical and abrasion resistance, good processibility, and protective barrier properties [2,3]. A typical TPU used in biomedical applications consists of poly(tetramethylene oxide) (PTMO) soft segment (SS), and a hard segment (HS) based on 4,4′-methylenebis(phenylisocyanate) (MDI) and 1,4-butanediol (BDO) as a chain extender (CE) [4]. The combination of diisocyanate and CE forms the HS and eventually the nano-phase segregation of HS and SS is responsible for the excellent mechanical properties of the TPUs. For example, PTMO diol (HO-PTMO-OH) based TPUs possess good ultimate tensile strength (UTS = 30–40 MPa) and elongation at break (350–600%) depending upon the ratio of HS:SS [5]. However, these polymers are highly susceptible to oxidative degradations leading to deterioration of mechanical properties [6]. The degradation has been assigned to cleavage of ether bonds in the SS of the TPU [7]. Therefore many efforts have focused on developing biostable TPUs, based on nonpolar macrodiols such as poly(dimethylsiloxane) (PDMS). However, PDMS based TPU exhibited low tensile strength (~7 MPa) and ultimate elongation (200%) [8]. The poor mechanical properties were attributed to the large difference between the solubility parameters of the HS and SS that leads to premature phase segregation during polymerization. The lack of soft segment crystallizability under strain has also been mentioned as another possible factor affecting the tensile properties of the resulting TPUs. In contrast Gunatillake et al. reported that mixed PDMS – polyhexamethylene diol (PHMO) based TPUs exhibit excellent UTS (~28 MPa), elongation at break (~580%) and Young's modulus (~33 MPa) [9].

Polyisobutylene (PIB) is well-known for its superior biostability and biocompatibility as many copolymers based on PIB have been synthesized and studied for various biomedical applications in recent times [10]. However, a PIB based TPU reported by Speckhard et al. showed low UTS (1–10 MPa) and inadequate elongation at break (10–200%) [11]. Similar results were reported for PIB TPUs with $M_n < 10{,}000$ g/mol by Mitzner et al. [12], who attributed the

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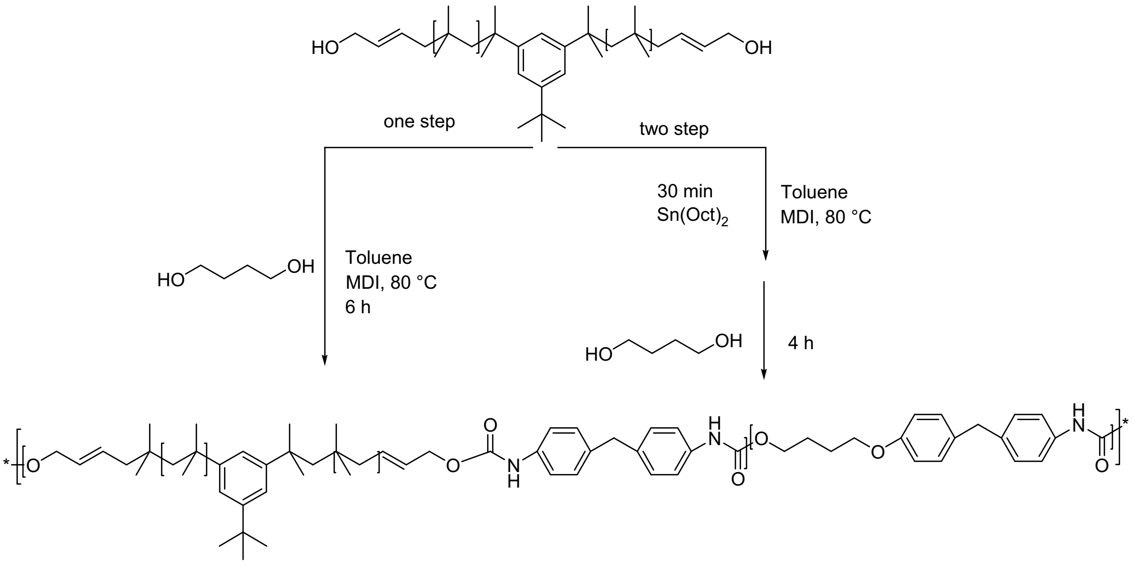


Scheme 1. Synthesis of polyisobutylene thermoplastic polyurethane using hydroxyallyl telechelic polyisobutylene (HO-Allyl-PIB-Allyl-OH), 4,4′-methylenebis(phenylisocyanate) (MDI) and 1,4-butanediol (BDO) by the one-step procedure (adding all reagents together) or two-step procedure (adding BDO as the last reagent).

poor mechanical properties to the absence of reinforcing H-bridges. Incorporation of even a small amount of PIB diols into polyether urethanes resulted in a significant decrease in tensile strength. For instance replacing 10 wt% of PTMO diol with PIB diol decreased the UTS from 23.4 MPa to 14.2 MPa [12].

The main objective of this work is to study the synthesis, processing and mechanical properties of PIB based polyurethanes that are expected to be resistant to biodegradation. The effect of reaction condition, catalyst and PTMO/PIB composition on the number averaged molecular weight (M_n), mechanical properties and processability is investigated.

2. Experimental

2.1. Materials

$Sn(Oct)_2$ (stannous octoate, Polyscience), 4,4′-methylenebis-(phenylisocyanate) (Aldrich, 98%), toluene (Aldrich, 99%), chloroform (Aldrich, ≥99.8%), 1,4-butanediol (Aldrich, 99%), LiBr (lithium bromide ReagentPlus, Aldrich, ≥99%), KOH (potassium hydroxide, Aldrich), Na_2SO_4 (sodium sulfate, Aldrich), trifluoroacetic acid (TFA, Aldrich), tetra-*n*-butylammonium bromide (TBAB, Alfa Aesar, 98+%) and poly(tetramethylene oxide) diol (TERATHANE® 1000 polyether glycol, Aldrich) were used as received. Pellethane™ 2363-80A and Pellethane™ 2363-55D were received from Dow Chemicals Co. Tetrahydrofuran (THF, Aldrich) or toluene were refluxed over sodium metal and benzophenone over night and distilled under nitrogen atmosphere prior to use. Hexanes were purified by refluxing over sulfuric acid for 24 h. They were washed with aqueous solution of KOH 3 times followed by distilled water. Then they were stored over sodium sulfate over night at room temperature. Finally they were distilled over CaH_2 under nitrogen atmosphere before use.

2.2. Measurements

^{1}H NMR spectroscopy for structural analysis was carried out on a Bruker 500 MHz spectrometer using a mixture of $CDCl_3$ (Cambridge Isotope Laboratories, Inc.) and CF_3COOD as a solvent. Molecular weights were measured with a Waters HPLC system equipped with a model 510 HPLC pump, model 410 differential refractometer, model 441 absorbance detector, online multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), Model 712 sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100Å. THF:TBAB (98:2, wt:wt) was used as a carrier solvent with a flow rate of 1 mL/min. ReactIR™ 4000 instrument (Mettler Toledo AutoChem, Inc.) was used to monitor the polyurethane synthesis. An AVATAR 370 FT-IR spectrometer was used to record the FT-IR spectra of the samples either in dry CCl_4 solutions or thin films on NaCl pellet. The data were corrected and analyzed on iC IR Software (2.0.150.2, Mettler Toledo AutoChem, Inc.). Buchi rotavapor was used to evaporate solvents under reduced pressure. Static tensile properties {Young's modulus, ultimate tensile strength

Table 1
Hard segment:soft segment ratio and Shore hardness data of PIB based TPUs.

Code	HO-Allyl-PIB-Allyl-OH (M_n, g/mol)[a]	MDI/BDO/PIB (molar ratio)	SS:HS (wt:wt)	Shore hardness (A)	M_n (g/mol) (GPC)	PDI (GPC)
PIB-4321	4200	3/2/1	81:19	60	110,000	2.3
PIB-2211	2200	2/1/1	79:21	59	92,000	3.1
PIB-1514[b]	1500	5/1/4	80:20	62	–	–
PIB-4761	4200	7/6/1	62:38	81	87,000	2.0
PIB-2431	2200	4/3/1	60:40	79	91,000	2.2
PIB-1321	1500	3/2/1	59:41	83	83,000	1.8

[a] The number average molecular weight was determined from ^{1}H NMR spectroscopy.
[b] PIB-1514 is not soluble in THF/TBAB mixture.

Table 2
M_n of PIB-2211 obtained after different reaction time.

Reaction time	M_n (g/mol, GPC)	PDI (GPC)
0[a]	2200	1.16
30 min	23,000	1.8
40 min	32,000	1.8
3 h	66,000	2.0
6 h	87,000	2.2
360 h[b]	105,000	2.4

[a] Represents M_n of precursor HO-Allyl-PIB-Allyl-OH.
[b] M_n of PIB-2211 obtained after curing for one week.

(UTS), and elongation} were measured at room temperature (~25 °C) and atmospheric conditions with a 50 lbs (220 N) load cell on an Instron Model Tensile Tester 4400R at 50 mm/min extension rate. All tests were carried out according to ASTM standard (ASTM D412). Samples were cut into dog-bone shape using an ASTM standard die. All samples were kept at room temperature and atmospheric conditions prior to testing. Tear strength of the polymers were measured using ASTM D624 half-size die. The polymers were compression molded at 160 °C for 10 min using 17,000–20,000 lb in a Carver model C press equipped with thermostatic temperature control and a load capacity of 12 ton. The sample was weighed (approximately 1.5 g) and placed within a thin rectangular aluminum mold on a teflon coated aluminum foil. The sample was covered with teflon coated aluminum foil and was then placed between the heated platens. The lower platen was raised and a load of about 20,000 lbs was applied. The load was released immediately and reapplied to enable venting of trapped air. After 8 minutes, the load was released and the sample was removed, put immediately in a dessicator and allowed to cool to room temperature. The film formed was then removed carefully from the aluminum foil. The DSC analysis of the block copolymers was carried out in a Q100 TA instrument. The samples were heated and cooled under nitrogen atmosphere. The sample size was maintained in between 4 and 8 mg. The heating rate was 10 °C/min unless otherwise noted. The data were recorded in "exo up" mode.

2.3. Synthesis

2.3.1. Syntheses of PIB based thermoplastic polyurethanes (one-step procedure)

A representative synthetic procedure for PIB-2211 is described below: HO-Allyl-PIB-Allyl-OH (M_n = 2200 g/mol, 5.2 g, 2.36 mmol) and BDO (212 mg, 2.36 mmol) were dried by azeotropic distillation using dry toluene (10 mL). The mixture was kept at 45 °C for 3 h under vacuum. To it 25 mL of dry toluene was added followed by $Sn(Oct)_2$ (20 mg, 0.05 mmol) in toluene. The mixture was heated at 80 °C under a slow stream of dry nitrogen gas. To it MDI (1.24 g, 4.96 mmol) was added and the mixture was stirred vigorously for 6 h. The mixture was cooled to room temperature, poured in a Teflon mold and the solvent was evaporated at room temperature in air for 48 h. Finally the polymer was dried under vacuum at 50 °C for 12 h. The following spectral data was obtained for a typical PIB TPU. ^1H NMR ($CDCl_3$, ppm, δ): 7.2 (s, Ar), 7.14 (s, Ar), 5.9 (p, $-CH{=}\boldsymbol{CH}-CH_2OCONH-$), 5.6 (p, $-\boldsymbol{CH}{=}CH-CH_2OCONH-$), 4.7 (s, p, $-CH{=}CH-\boldsymbol{CH_2}OCONH-$), 4.3 (s, $-HN-COO-\boldsymbol{CH_2}-$), 3.95 (s, $-C_6H_4-\boldsymbol{CH_2}-C_6H_4-$), 2.0 (d, 2H, $C(CH_3)_2\boldsymbol{CH_2}CH{=}$), 1.5–14 (br, $-\boldsymbol{CH_2}C(CH_3)_2-$), 1.2–1.1 (br, $-CH_2C(\boldsymbol{CH_3})_2-$). FT-IR (thin film, cm^{-1}): 3324 ($-N-H_{str}$, urethane linkage), 2951 ($-C-H_{str}$, $-CH_2$ and CH_3), 1704 ($-C{=}O_{str}$, urethane linkage), 1224 ($-C-O_{str}$, urethane linkage).

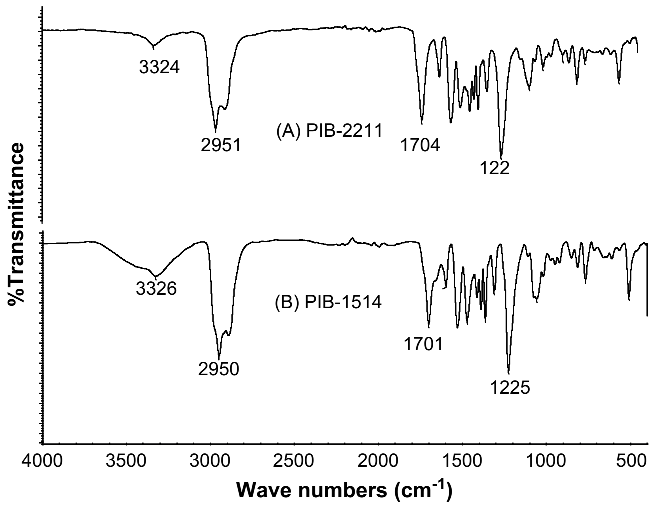


Fig. 1. FT-IR spectra of polyisobutylene based thermoplastic polyurethanes (A) PIB-2211 and (B) PIB-1514 (Shore hardness ≈ 60 A).

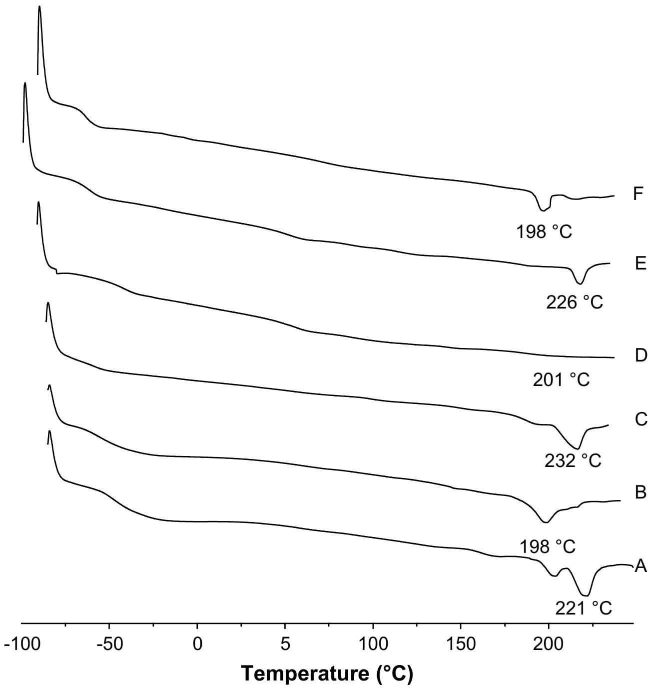


Fig. 2. Differential scanning calorimetry heating scans of polyisobutylene based thermoplastic polyurethanes; the T_ms of the polymers are identified in the traces. PIB-1321 (A), PIB-2431 (B), PIB-4761 (C), PIB-1514 (D), PIB-2211 (E), PIB-4321 (F).

Table 3
DSC and tensile data of PIB based TPUs.

Polymer	T_{g1} (°C)[a]	T_{g2} (°C)[b]	T_{m2}	T_{m3}	Young's modulus (MPa)	UTS (MPa)	Elongation at break (%)
PIB-4321	−62.5	71.03	198	–	6	7	200–250
PIB-4761	−66.0	–	193, 217	232	40	6	30–40
PIB-2211	−53.4	62.0	–	226	5	9	300–400
PIB-2431	−56.1	60.2	198, 210	216	–	–	–
PIB-1514	−44.4	57.2	201	–	5	6	100–150
PIB-1321	−46.0	56.3	170, 202	221	–	–	–

[a] T_{g1}: Glass transition of PIB segment.
[b] T_{g2}: Glass transition of MDI–BDO hard segment.

Table 4
Tensile properties of PIB-2211 synthesized using $Sn(Oct)_2$ or DTDS.

Polymer[c]	Shore A	Young's modulus (MPa)	UTS (MPa)	Elongation at break (%)
PIB-2211-$Sn(Oct)_2$	59	5	9	300–400
PIB-2211[a]-DTDS	60	24	12	100
PIB-2431-$Sn(Oct)_2$[b]	–	–	–	–
PIB-2431[a]-DTDS	80	72	15	30–40

[a] Not soluble in THF/TBAB, soluble in THF/TFA.
[b] The polymer did not form uniform films under compression-molding conditions.
[c] The polymers were synthesized by one-step procedure.

2.3.2. *Synthesis of PIB based thermoplastic polyurethane (two-step procedure)*

A representative synthetic procedure for PIB-4321 is described below: HO-Allyl-PIB-Allyl-OH ($M_n = 4200$ g/mol, 5.2 g, 1.24 mmol) was dried by azeotropic distillation using dry toluene (10 mL). The polymer was kept at 45 °C for 3 h under vacuum. To it 25 mL of dry toluene was added followed by $Sn(Oct)_2$ (15 mg, 0.037 mmol) in toluene. The mixture was heated at 80 °C under a slow stream of dry nitrogen gas. To it MDI (930 mg, 3.72 mmol) was added and the mixture was stirred vigorously for 30 min. To it BDO (223 mg, 2.48 mmol) was added and stirring continued for 4 h. The mixture was cooled to room temperature, poured in a Teflon mold and the solvent was evaporated at room temperature in air for 48 h. Finally the polymer was dried under vacuum at 50 °C for 12 h.

2.3.3. *Syntheses of PIB and PTMO based thermoplastic polyurethanes (two-step procedure)*

A representative synthetic procedure for PIB-PTMO-82-6 is described below: HO-Allyl-PIB-Allyl-OH ($M_n = 2200$ g/mol, 5.2 g, 2.36 mmol) and PTMO ($M_n = 1000$ g/mol, 1.3 g, 1.3 mmol) were dried by azeotropic distillation using dry toluene (10 mL). The mixture was kept at 45 °C for 3 h under vacuum. To it 25 mL of dry toluene was added followed by $Sn(Oct)_2$ (28.3 mg, 0.07 mmol) in toluene. The mixture was heated at 80 °C under a slow stream of dry nitrogen gas. To it MDI (1.76 g, 7.02 mmol) was added and the mixture was stirred vigorously for 30 min. To it BDO (302 mg, 3.36 mmol) was added and the mixture was stirred for 4 h at 100 °C. The mixture was cooled to room temperature, poured in a Teflon mold and the solvent was evaporated at room temperature in air for 48 h. Finally the polymer was dried under vacuum at 50 °C for 12 h. ^{1}H NMR ($CDCl_3$, ppm, δ): 7.2 (s, Ar), 7.14 (s, Ar), 5.9 (p, $-CH{=}\boldsymbol{CH}-CH_2OCONH-$), 5.6 (p, $-\boldsymbol{CH}{=}CH-CH_2OCONH-$), 4.7 (s, p, $-CH{=}CH-\boldsymbol{CH_2}OCONH-$), 4.3 (s, $-HN-COO-\boldsymbol{CH_2}-$), 3.95 (s, $-C_6H_4-\boldsymbol{CH_2}-C_6H_4-$), 3.66 (s, $-O-\boldsymbol{CH_2}-$PTMO), 2.0 (d, 2H, $C(CH_3)_2\boldsymbol{CH_2}CH{=}$), 1.5–1.4 (br, $-\boldsymbol{CH_2}C(CH_3)_2-$), 1.2–1.1 (br, $-CH_2C(\boldsymbol{CH_3})_2-$).

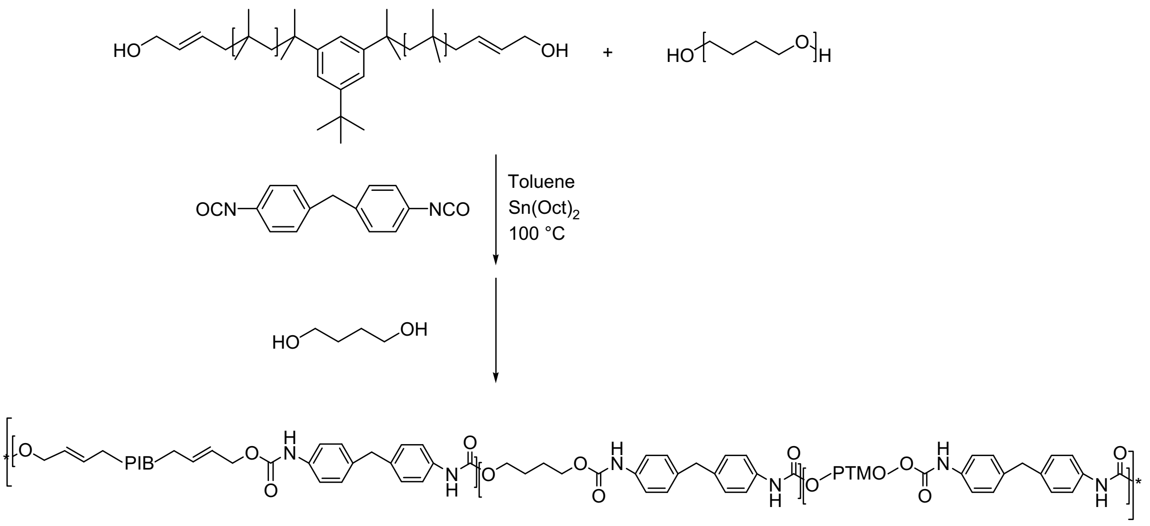
3. Results and discussion

Three low molecular weight hydroxyallyl telechelic PIBs ($M_n = 4400$ g/mol, PDI = 1.20, $M_n = 2300$ g/mol, PDI = 1.16 or $M_n = 1600$ g/mol, PDI = 1.18) were synthesized by hydrolysis of bromoallyl telechelic PIB at elevated temperature as reported before [13]. The PIB macrodiols along with MDI were chain extended with BDO to obtain the corresponding TPUs as shown in Scheme 1. Toluene was used as the solvent for all polyurethane synthesis.

3.1. *Synthesis of PIB TPUs (one-step procedure)*

Two sets of PIB based TPUs with designed Shore hardness of ~60 A (HS:SS ratio ≈ 20:80 wt:wt) and ~80 A (HS:SS ratio ≈ 35:65 wt:wt) were synthesized using the one-step (MDI was added last) procedure (Table 1).

In-situ FT-IR spectroscopy was used to determine the extent of chain extension by monitoring the increase in intensity of $-C{=}O_{str}$ (urethane linkage) band at 1700 cm^{-1}. However, a significant increase in peak intensity was noticeable only up to 40 min ($M_n = 32{,}000$ g/mol, PDI = 1.8) after which the plateau was reached (Supplementary information). Therefore the reaction time was further optimized by collecting and measuring the M_n of aliquots after regular time interval. In case of PIB-2211, an increase in M_n from 23,000 g/mol/30 min to 87,000 g/mol/6 h was observed with time. The TPU was then cured for a week at room temperature. A further increase in M_n to 105,000 g/mol, (PDI = 2.4) of the cured sample indicated post-polymerization curing is necessary to obtain polymers with higher M_n as shown in Table 2. Similar reaction time (6 h) and post-polymerization processing conditions were employed for the synthesis of other TPUs. The ^{1}H NMR spectra showed the disappearance of peaks at 4.15 ppm for $={CH}\boldsymbol{CH_2}OH$



Scheme 2. Synthesis of hydroxyallyl telechelic polyisobutylene/polytetramethylene oxide diol/4,4′-methylenebis(phenylisocyanate)/1,4-butanediol (BDO) based thermoplastic polyurethane by the two-step procedure (BDO was added as the last reagent).

and a new resonance at 4.7 ppm accountable to $-CH{=}CH-\boldsymbol{C}\boldsymbol{H}_2O$-CONH– indicated successful chain extension (Supplementary information). New peaks at 5.6, 3.95 and 5.9 ppm for $-\boldsymbol{C}\boldsymbol{H}{=}CH-CH_2OCONH-$, $-C_6H_4-\boldsymbol{C}\boldsymbol{H}_2-C_6H_4-$ and $-CH{=}\boldsymbol{C}\boldsymbol{H}-CH_2O$-CONH– supported the formation of TPUs. The FT-IR spectra of the polymers showed a strong band at 1700 cm^{-1} accountable to the $-C{=}O_{str}$ of urethane linkage and the $-N-H_{str}$ frequency was observed around 3300 cm^{-1} for all the TPUs (Fig. 1). The polymers were soluble in various solvent mixtures such as THF:TBAB (98:2, wt:wt), TFA:chloroform (10:90, v:v) and xylene:DMF (80:20, v:v) (Supplementary information). The GPC analysis of polymers in THF containing 2 wt% TBAB showed M_n in the range of 83,000–110,000 g/mol with PDI ≈ 1.8–3.1 (Table 1).

3.2. DSC analysis of PIB TPUs

The DSC endotherms were used to understand various thermal transitions associated with the TPUs. The heating traces showed distinct T_gs for the SS in the range of −44 to −60 °C and for the HS in the range of 56–71 °C. This indicated microphase separation of the immiscible segments in the polymers [14]. However, with the decrease in M_n of the PIB segment an increase in T_g of the SS and a decrease in T_g of the HS was noticed, which suggests partial phase mixing (Table 4) [15]. The hard – MDI–BDO – segments are crystalline and exhibit melting temperatures above 100 °C. The multiple melting peaks observed corresponded to the length of the MDI–BDO segment [16]. For instance, the MDI–BDO–MDI segments exhibit melting temperatures between 100 °C and 180 °C (T_{m1}). Longer segments such as MDI–BDO–MDI–BDO and MDI–BDO–MDI–BDO–MDI have higher melting peaks in the range of 180–210 °C (T_{m2}) and 211–240 °C (T_{m3}), respectively (Fig. 2). The position of the melting peak also signified the interactions between the two phases. Higher T_ms indicated a more phase segregated morphology. Table 3 lists the melting temperatures of the PIB TPUs for Shore 60 A and 80 A hardness. As could be seen from Table 3 and Fig. 2 the T_{m1} melting peak, which lies between 100 °C and 180 °C corresponding to the MDI–BDO–MDI interactions, is absent in the PIB TPUs. This phenomenon demonstrated a premature phase segregation of the segments during synthesis resulting in formation of longer SS and HS. Hence the TPUs exhibited poor processing and mechanical behavior.

3.3. Tensile properties of PIB TPUs

The UTS of the compression-molded films of TPUs (Shore hardness ≈ 60 A) were obtained in the range of 6–9 MPa with ∼150–400% elongation at break (Table 3). These values were similar to those reported previously for PIB TPUs [11]. With a further increase in HS content (Shore hardness 80 A), the polymer become very brittle and the ultimate elongation decreased significantly (∼30%). The thermal processing of PIB-2431 and PIB-1321 was not possible as the compositional heterogeneity further increased affecting the melt-flow behavior and these TPUs could not be compression molded into flat sheets for testing. As expected Young's modulus of the TPUs increased with increasing hardness from ∼5 MPa (Shore 60 A) to 40 MPa (Shore 80 A). TPUs based on HO-Allyl-PIB-Allyl-OH (M_n = 2200 g/mol) possessed the maximum tensile properties in terms of UTS ≈ 9 MPa and ultimate elongation ≈ 400%.

3.4. Effect of catalyst

The effect of catalyst was studied by comparing the TPUs synthesized using the one-step procedure with $Sn(Oct)_2$ or 1,3-Diacetoxy-1,1,3,3-tetrabutyldistannoxane (DTDS). The TPUs synthesized using DTDS were yellow in color and lacked solubility in THF:TBAB mixture. With DTDS, the UTS of PIB-2211 increased to 12 MPa (from 9 MPa with $Sn(Oct)_2$) and the elongation at break decreased from 350% to 100% as depicted in Table 4. The PIB-2431 sample synthesized with DTDS showed UTS of 15 MPa with 40% ultimate elongation whereas the TPU obtained with $Sn(Oct)_2$ could not be compression molded.

Table 5
PIB and PTMO wt% and M_n data of PIB-PTMO TPUs.

Code	HO-PIB-OH[a] (wt % in SS)	HO-PTMO-OH[b] (wt % in SS)	PTMO wt%[c]	M_n (g/mol, GPC)	PDI (GPC)	Shore A[d]
PIB-PTMO-91-6	90	10	8	94,000	2.1	71
PIB-PTMO-82-6	80	20	16	129,000	2.2	60
PIB-PTMO-73-6	70	30	24	137,000	2.7	61
PIB-PTMO-64-6	60	40	32	95,000	2.2	59
PIB-PTMO-55-6	50	50	40	85,000	1.4	62
PIB-PTMO-28-6	20	80	64	55,000	1.6	60
PTMO-60A	0	100	80	31,000	1.3	61
PIB-PTMO-91-8	90	10	6.5	84,000	1.9	83
PIB-PTMO-82-8	80	20	13	119,000	2.8	82
PIB-PTMO-73-8	70	30	19.5	138,000	3.5	81
PIB-PTMO-64-8	60	40	26	130,000	3.7	81
PIB-PTMO-28-8	20	80	52	40,000	3.8	80
PTMO-80A	0	100	65	42,000	2.4	79
PIB-PTMO-91-9	90	10	6	–	–	95
PIB-PTMO-82-9	80	20	12	87,000	3.4	98
PIB-PTMO-73-9	70	30	18	79,000	1.6	99
PIB-PTMO-64-9	60	40	24	105,000	2.5	98
PIB-PTMO-55-9	50	50	30	111,500	2.8	96
Pellathane-55D	0	100	–	119,000	1.7	98

[a] HO-PIB-OH, M_n = 2200 g/mol.
[b] HO-PTMO-OH, M_n = 1000 g/mol.
[c] PTMO wt% in TPU.
[d] Shore hardness = 60–71 A have HS:SS = 20:80 wt:wt, Shore hardness = 80–83 A have HS:SS = 35:65 wt:wt and Shore hardness = 95–99 A have HS:SS = 30:60 wt:wt.

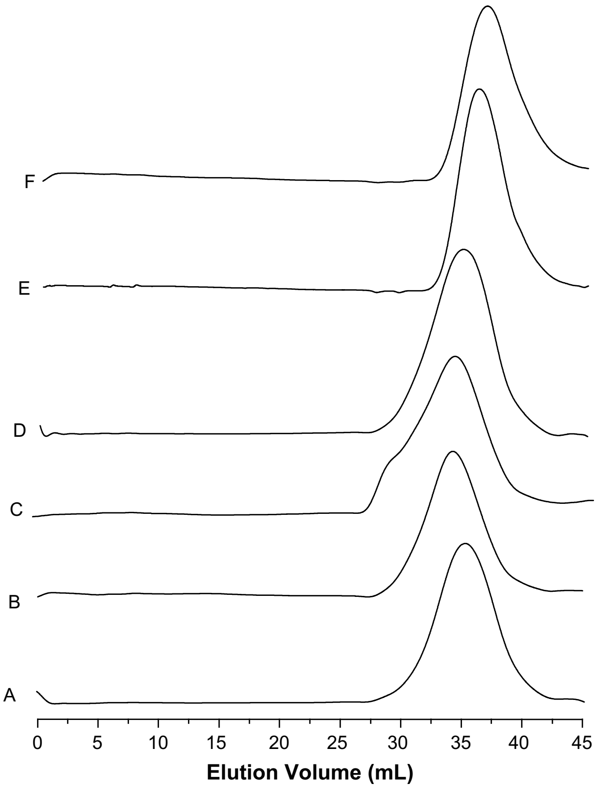


Fig. 3. GPC-RI traces of polyisobutylene–polytetramethylene oxide thermoplastic polyurethanes (Shore hardness ≈ 60 A) PIB-PTMO-91-6 (A), PIB-PTMO-82-6 (B), PIB-PTMO-73-6 (C), PIB-PTMO-64-6 (D), PIB-PTMO-55-6 (E) and PIB-PTMO-28-6 (F).

3.5. Two-step procedure

To achieve better mixing of SS and HS the synthetic procedure was modified by preparing the MDI capped PIB in the first step followed by in-situ chain extension with BDO in the consecutive step to obtain the final polymer (Scheme 1). PIB-4321 was synthesized by the two-step method and the thermal and tensile properties were compared with that of the same polymer synthesized by the one-step procedure. The M_n (119,000 g/mol) of the TPU obtained in the two-step procedure was higher compared to that of the one-step method ($M_n = 110{,}000$ g/mol) and the PDI decreased (Supplementary information). As expected, the DSC analysis showed a decrease in T_m of the hard segment formed by the two-step method and the thermal processing was easier as the TPU formed uniform films. However, the tensile properties were similar in both cases (Supplementary information).

The above studies indicated that the thermo-mechanical properties of PIB based TPUs are not comparable to conventional TPUs. The low miscibility of the two segments results in phase segregation during synthesis leading to highly heterogeneous microstructure. To overcome this problem, a polar macrodiol, HO-PTMO-OH was incorporated into the soft segment and the mechanical properties were examined.

3.6. Synthesis of TPUs based on PIB and PTMO (Shore hardness ≈ 60 A, 80 A and 95 A)

Three series of TPUs with varying PIB:PTMO ratios were synthesized using the two-step synthetic procedure. The ratio of SS:HS ≈ 80:20, 65:35 and 60:40 wt:wt was maintained for a particular series to obtain polymers with Shore ≈ 60 A, 80 A or 95 A hardness respectively (Scheme 2). The nomenclature of the TPUs along with the PIB:PTMO ratio is depicted in Table 5. The ratio of PIB:PTMO was varied in each series from 90:10 to 20:80 wt:wt in the SS (Table 5).

After polymerization all polymers were kept at room temperature for 48 h followed by 12 h under vacuum at 50 °C. In the ^{1}H NMR spectra, the peak at 4.15 ppm attributed to the hydroxymethylene proton of PIB macrodiol disappeared and a new resonance at 4.7 ppm appeared for $-C\boldsymbol{H}_2OCONH-$ indicating successful polyurethane synthesis. New resonances at 3.95 and 4.3 ppm assigned to $C_6H_4-C\boldsymbol{H}_2-C_6H_4-$ and $-NHCOOC\boldsymbol{H}_2C_3H_6O-$ were also observed indicating the incorporation of MDI and BDO unit in the polymer backbone (Supplementary information). The oxymethylene protons of PTMO repeating unit resonated at 3.7 ppm. The FT-IR spectra showed bands at ~1704 and ~3324 cm^{-1} for the $-C{=}O_{str}$ and $-N-H_{str}$ of urethane linkage. All polymers except PIB-PTMO-91-9 were soluble in various solvent mixtures such as $CHCl_3$:TFA (80:20, v:v, rt) and THF:TBAB (98:2, wt:wt, 50 °C) (Supplementary information). The GPC analysis of PIB–PTMO TPU were carried out in THF:TBAB (98:2, wt:wt) at room temperature. In case of TPUs with 60 A Shore hardness, all polymers showed monomodal distribution of molecular weight except PIB-PTMO-73-6, which exhibited a small hump at a lower elution volume (Fig. 3).

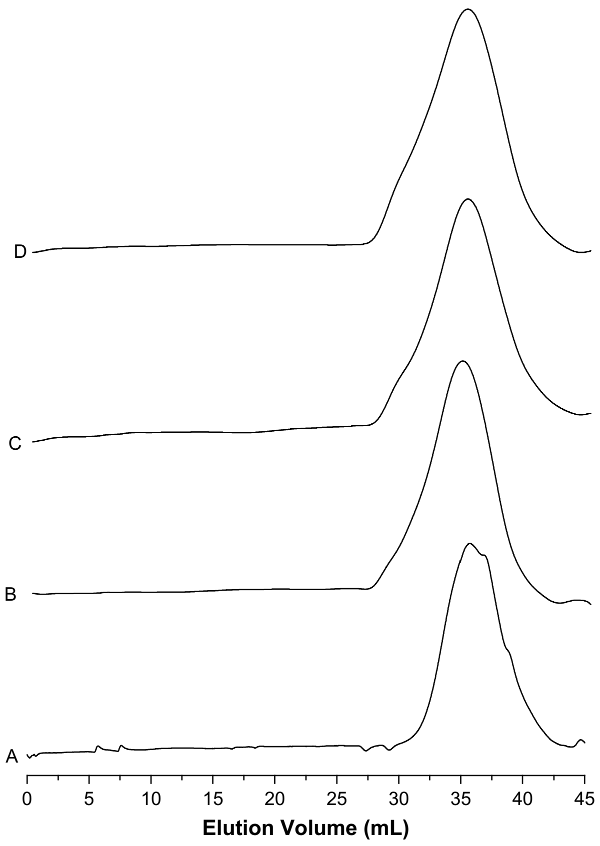


Fig. 4. GPC-RI traces of polyisobutylene-polytetramethylene oxide thermoplastic polyurethanes (Shore hardness ≈ 80 A). PIB-PTMO-91-8 (A), PIB-PTMO-82-8 (B), PIB-PTMO-73-8 (C), PIB-PTMO-64-8 (D).

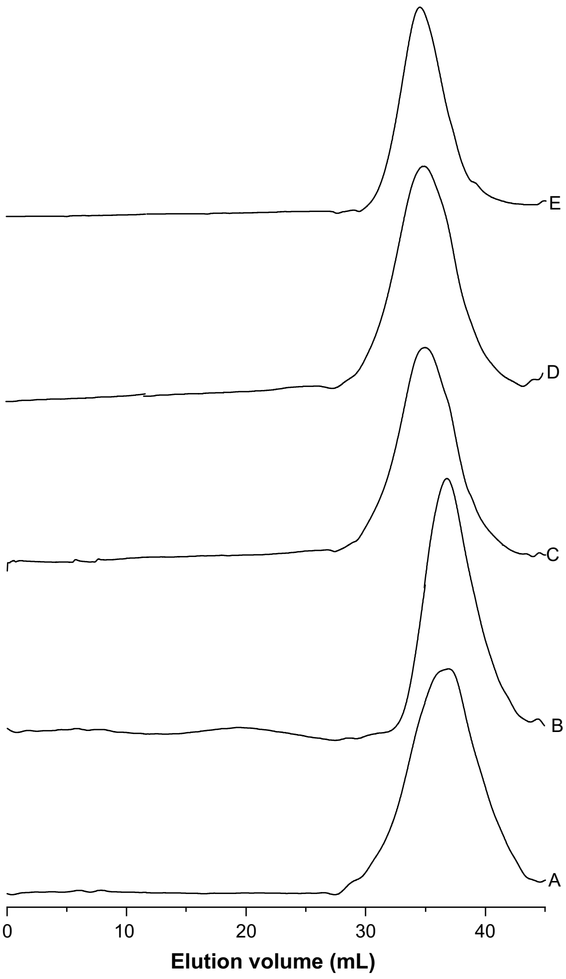


Fig. 5. GPC-RI traces of polyisobutylene–polytetramethylene oxide thermoplastic polyurethanes (Shore hardness ≈ 95 A). PIB-PTMO-82-9 (A), PIB-PTMO-73-9 (B), PIB-PTMO-64-9 (C), PIB-PTMO-55-9 (D), Pellathane-55D (E).

Table 6
DSC and tensile data of PIB-PTMO TPUs (Shore hardness ≈ 60 A).

Polymer	T_{g1} (°C)	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	Young's modulus (MPa)	UTS (MPa)	Elongation at break (%)	Tear strength (N/mm)
PIB-PTMO-91-6	−61	156	188	234	8.5	20	400	38.5
PIB-PTMO-82-6	−59	144	187	–	5.2	18	680	53.9
PIB-PTMO-73-6	−51	166	188	238	4.5	18	740	52.5
PIB-PTMO-64-6	−49	145	183	225	4.7	22	740	–
PIB-PTMO-55-6	−48	–	186	226	7.5	22	730	58.1
PIB-PTMO-28-6	−54	145	–	232	2	4	400	–

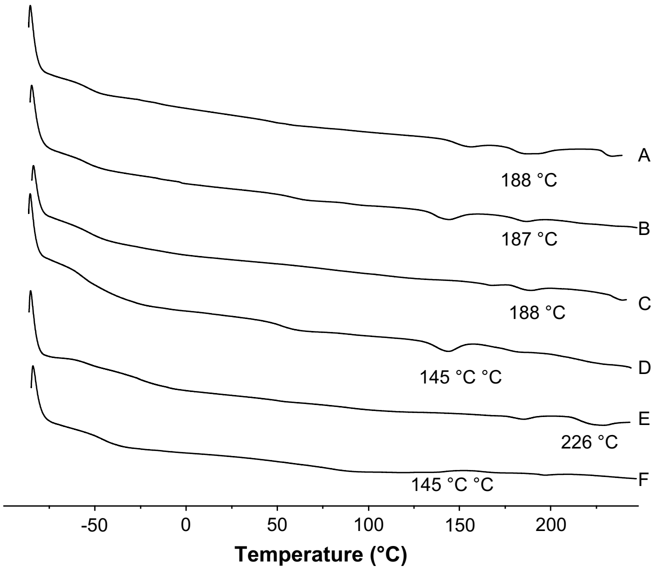


Fig. 6. Differential scanning calorimetry heating scans of polyisobutylene–polytetramethylene oxide thermoplastic polyurethanes (Shore hardness ≈ 60 A). PIB-PTMO-91-6 (A), PIB-PTMO-82-6 (B), PIB-PTMO-73-6 (C), PIB-PTMO-64-6 (D), PIB-PTMO-55-6 (E), PIB-PTMO-28-6 (F).

The M_ns were obtained in the range of 55,000–137,000 g/mol with PDI ≈ 1.4–2.7 (Table 5). The GPC-RI traces of the PIB–PTMO TPUs with 80 A Shore hardness are depicted in Fig. 4. The TPUs exhibited M_n in the range of 84,000–138,000 g/mol with PDI = 1.7–3.7 (Table 5). Similarly, GPC-RI traces of the TPUs with 95 A Shore hardness were monomodal with M_n in the range of 79,000–111,000 g/mol and PDI = 1.6–3.4 (Fig. 5, Table 5). The $M_n = 119{,}000$ g/mol of commercial TPU (Pellathane™ 55D) was in the same range with relatively low PDI = 1.7. However, TPUs with PTMO wt% > 50 in SS exhibited significantly lower M_n (=31,000–55,000 g/mol, PDI = 1.3–3.8). This was attributed to the incompatibility of solvent (toluene) with the polar PTMO macrodiol and chain extender as the polymers precipitated prematurely before reaching a high M_n.

3.7. DSC analysis of PIB–PTMO TPUs

The DSC heating data of PIB–PTMO TPUs (Shore 60 A) containing varying ratios of PIB:PTMO are summarized in Table 6. All polymers except PIB-PTMO-55-6 exhibited T_{m1} corresponding to the melting of MDI–BDO–MDI segments. The lowering of the melting peaks with respect to TPUs based on PIB segment indicated that the addition of PTMO diol improved the miscibility of the soft and the hard segments. Even a small amount of PTMO diol (10–20 wt% in SS) was sufficient to provide the necessary interactions. However, other melt endotherms at higher temperatures were also observed indicating the presence of higher order HS in the polymers (Fig. 6). Interestingly for PIB-PTMO-64-6 a broader endotherm at ∼54 °C was observed which could be attributed to a low degree of HS ordering resulting from the annealing of the sample at room temperature [17]. Most of the TPUs also exhibited two T_gs at −60 and 50 °C for the SS and HS, respectively, indicating microphase segregated morphology. Table 7 and Fig. 7 illustrate the melting peaks of the PIB–PTMO TPUs (Shore 80 A). Though all the TPUs showed multiple melting endotherms T_{m2} was the most prominent. This phenomenon was expected since the HS content is increased in this case compared to PIB–PTMO TPUs with 60 A Shore hardness which showed T_{m1} as the prominent peak. Multiple endotherms in the range of 215–240 °C were also observed for the TPUs indicating the presence of – MDI$_5$BDO$_4$ – (T_{m4}) and – MDI$_6$BDO$_5$ – (T_{m5}) sequences in the polymers. However, the enthalpy of those peaks was low. The control TPU based on PTMO segment (PTMO-80A) showed the main T_{m1} at 151 °C. This is due to the uniform distribution of HS and SS arising from the good miscibility of PTMO with HS (MDI–BDO) during synthesis. The T_{g1} for the PTMO segment in PTMO-80A was observed at −38 °C. The DSC analysis of PIB–PTMO TPUs (Shore hardness ≈ 95 A) also exhibited T_{g1} (∼−60 °C) and T_{g2} (∼50 °C) along with T_{m1} (157–180 °C) and T_{m2} (190–220 °C) though T_{m3} was absent in all cases (Fig. 8 and Table 8). A broad peak at 100 °C was also observed for some TPUs indicating ordering of the HS domain.

3.8. Tensile properties of PIB–PTMO TPUs

The static tensile properties of PIB–PTMO TPUs are given in Table 6–8. The PIB–PTMO TPUs with 60 A Shore hardness exhibited a significant increase in the UTS compared to PIB TPUs having similar Shore hardness (Table 6). The impact of addition of PTMO is clearly seen in the UTS (∼20 MPa) as well as in the ultimate elongations (∼700 MPa). The maximum elongation has increased dramatically with the addition of PTMO. Optimum tensile properties in terms of the strength and modulus are obtained for PIB-PTMO-91-6 which contains just 10 wt% PTMO in SS. Further increase in PTMO wt% resulted in similar UTS and Young's

Table 7
DSC and tensile data of PIB–PTMO TPUs (Shore hardness ≈ 80 A).

Polymer	T_{g1} (°C)	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	Young's modulus (MPa)	UTS (MPa)	Elongation at break (%)	Tear strength (N/mm)
PIB-PTMO-91-8	−59	179	201	235	32	18	150	54.3
PIB-PTMO-82-8	−57	–	190, 210	232	32	23	400	66.5
PIB-PTMO-73-8	−56	–	187	219, 231	23	27	370	73.5
PIB-PTMO-64-8	−57	180	204	224	11	25	550	77.0
PIB-PTMO-28-8	−52	–	194	217,231	5	8	550	47.2
PTMO-80A	−38	151, 177	204	226	–	–	–	–

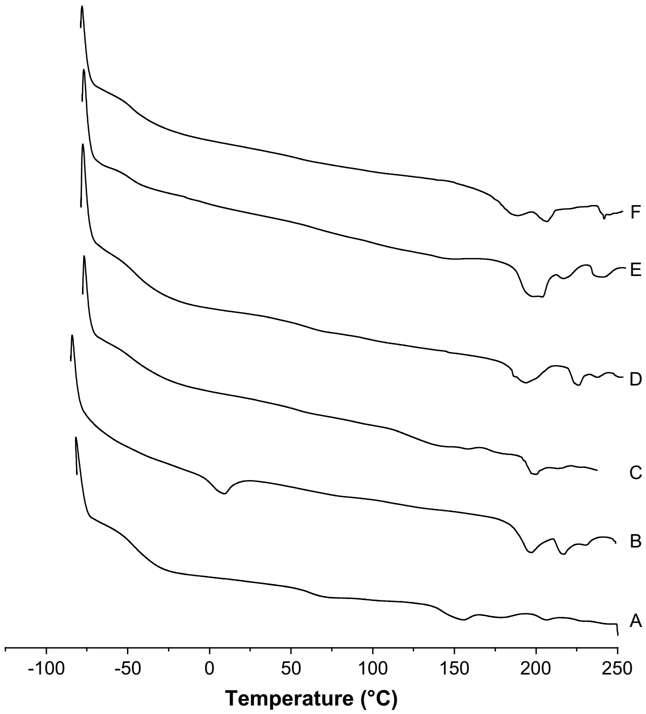


Fig. 7. Differential scanning calorimetry heating scans of polyisobutylene–polytetramethylene oxide thermoplastic polyurethanes (Shore hardness ≈ 80 A). PTMO-80A (A), PIB-PTMO-28-8 (B), PIB-PTMO-64-8 (C), PIB-PTMO-73-8 (D), PIB-PTMO-82-8 (E), PIB-PTMO-91-8 (F).

modulus, which was also comparable to the TPU based on PTMO. The tear strength of the TPUs was observed in the range of 38.5–57.8 N/mm (Table 6). The tensile data of the PIB–PTMO TPUs agree well with the DSC data. A decrease in the melting temperature indicated an improvement in compositional homogeneity, which

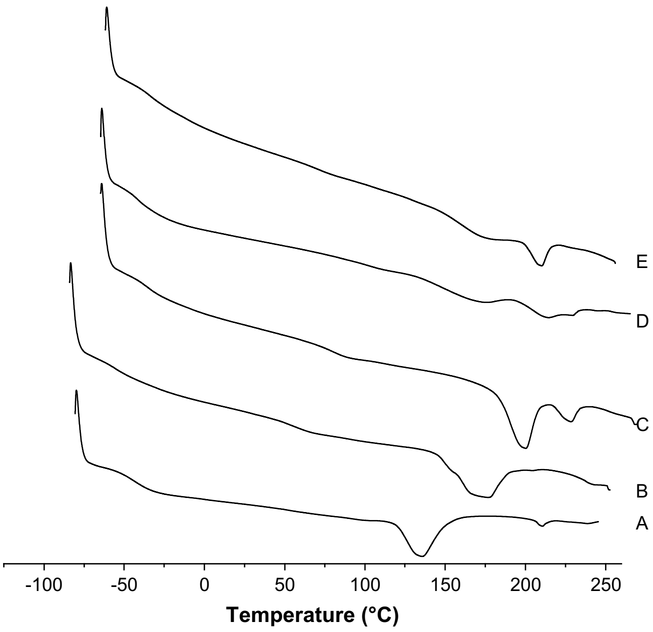


Fig. 8. Differential scanning calorimetry heating scans of polyisobutylene–polytetramethylene oxide thermoplastic polyurethanes (Shore hardness ≈ 95 A). Pellathane-55D (A), PIB-PTMO-55-9 (B), PIB-PTMO-64-9 (C), PIB-PTMO-73-9 (D), PIB-PTMO-82-9 (E).

Table 8
DSC analysis and tensile properties of PIB–PTMO TPUs (Shore hardness ≈ 95 A).

Polymer	T_{g1} (°C)	T_{g2} (°C)	T_{m1} (°C)	T_{m2} (°C)	UTS (MPa)	Young's modulus (MPa)	Elongation at break (%)
PIB-PTMO-91-9	−58.8	46.4	–	219.9	14	144	30
PIB-PTMO-82-9	−61.7	53.5	157.3	196.6	29	50	310
PIB-PTMO-73-9	−62.3	55.1	–	190.7, 212.2	40	45	350
PIB-PTMO-64-9	−57.4	54.0	180.5	209.4	39	27	430
PIB-PTMO-55-9	−62.1	53.0	175.3	–	42	17	510
Pellathane-55D	−42.2	–	138.2	211.3	44	16	400

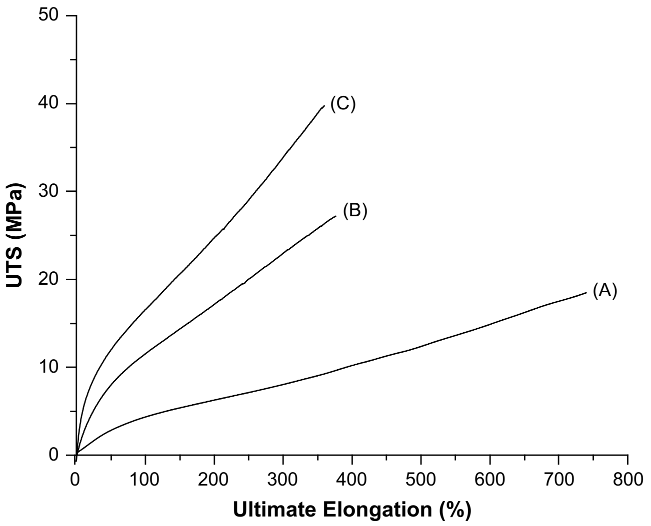


Fig. 9. Stress versus strain graph of (A) polyisobutylene (PIB)–polytetramethylene oxide (A) =PIB-PTMO-73-6 (Shore hardness ≈ 60 A), (B) =PIB-PTMO-73-8 (Shore hardness ≈ 80 A) and (C) =PIB-PTMO-73-9 (Shore hardness ≈ 95 A).

Table 9
GPC data of PIB–PTMO TPU (PTMO wt% ≥ 80 in SS) synthesized at 120 °C.

Code	M_n (g/mol, GPC)	PDI (GPC)	UTS (MPa)	Elongation at break (%)	Young's modulus (MPa)
PIB-PTMO-28-6	105,000	2.3	22	950	7
PTMO-60A	113,000	2.0	20	700	5
PIB-PTMO-28-8	87,000	1.8	17	740	9
PTMO-80A	102,000	1.7	35	800	7

Table 10
Tensile properties of PIB–PTMO TPUs and commercial PTMO TPUs.

Code[b]	Shore A	UTS (MPa)	Young's modulus (MPa)	Elongation at break (%)
PIB–PTMO TPU	61	18	4.5	740
PTMO-60A[d]	60	20	5	700
PIB–PTMO TPU	81	27	23	370
Pellethane™ 80A (measured[a]/Dow[e])	80/81	35/36	8/NA[c]	640/550
PTMO-80A[d]	80	35	7	800
PIB–PTMO TPU	95	40	45	350
Pellethane™ 98A (measured/Dow)	98/55D	44/47.5	16/NA	400/390

[a] Measured by us.
[b] Reported by manufacturer.
[c] Not available.
[d] The polymers were synthesized at 120 °C.
[e] All the PIB–PTMO TPU have 70:30 (wt:wt) PIB:PTMO in SS.

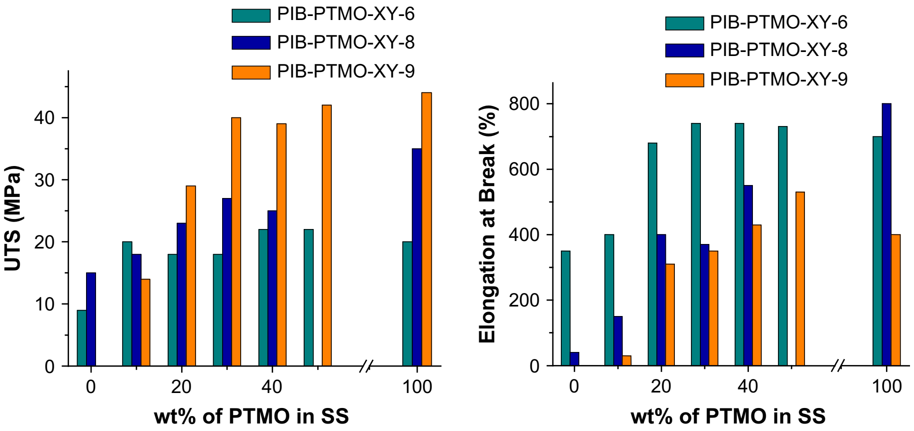


Fig. 10. Correlation of UTS and % elongation with polytetramethylene oxide (PTMO) wt% in case of polyisobutylene (PIB)-PTMO TPU. PIB-PTMO-XY-6, PIB-PTMO-XY-8 and PIB-PTMO-XY-9 represent TPUs with ~60 A, 80 A and 95 A Shore hardness respectively. The TPU with PIB/PTMO = 100/0 (wt% in SS, Shore A = 60) was synthesized by one-step procedure. The TPU with PIB:PTMO = 100:0 (wt:wt in SS, Shore A = 80) was synthesized by one-step procedure using DTDS as catalyst and TPU with PIB:PTMO = 0:100 (wt:wt in SS, Shore A = 98) was commercially obtained from Dow chemicals, i.e. Pellathane™ 2363-55D.

in turn resulted in excellent tensile properties. The thermal processing of these TPUs was also adequate as all the polymers formed uniform films under compression-molding conditions. Further enhancement in Young's modulus of these polyurethanes can be achieved by simply increasing the hardness of the polymer as discussed below.

Table 7 gives the static tensile properties and the tear strengths of PIB–PTMO TPU with higher hardness (Shore 80 A). Compared to Shore 60 A TPUs prominent enhancements are observed in Young's modulus and tear strengths, with an expected decrease in the ultimate elongation. Using 10 wt% PTMO in the SS increased the ultimate elongation to 150% compared to PIB-2431 which broke at 40% elongation. A further increase in PTMO content also increased the UTS and ultimate elongation of the polymers (Table 7). As expected the tear strengths (54–77 N/mm) were higher compared to PIB–PTMO TPUs with Shore 60 A hardness. Interestingly, Young's modulus value decreased from 32 MPa (PIB-PTMO-91-8) to 11 MPa (PIB-PTMO-64-8) with the increase in PTMO wt% in the polymer indicating that Young's modulus is directly proportional to the PIB content in TPUs having similar HS:SS wt:wt ratio. In case of PIB–PTMO TPUs with 95 A Shore hardness, the UTS reached the optimum value with 30 wt% PTMO in SS whereas the maximum elongation at break was reached at 40 wt% PTMO in SS (Table 8). The UTS and elongation at break was comparable to PTMO based commercial TPU (Pellathane™ 55D) with similar Shore hardness. Young's modulus was proportional to the PIB wt% in the SS as was observed for TPUs with 80 A Shore hardness. As expected the UTS and tear strength (82 N/mm) of the TPU were higher compared to the PIB–PTMO based TPUs with lower hardness (Shore 60 A and 80 A) (Fig. 9).

3.9. *Modification in procedure for higher PTMO wt% TPUs*

PIB–PTMO TPU with PTMO wt% > 50 in the SS reported using the two-step procedure failed to produce polymers with high M_n and hence the tensile properties were also inferior compared to their analogous TPUs with higher PIB wt%. Therefore the synthetic procedure was modified in order to achieve high M_n polymers with PTMO wt% > 50 in the SS. After the addition of BDO the temperature was increased to 120 °C to evaporate the solvent. The mixture was then cured at 100 °C for 4 h in the reaction vessel. The GPC analysis of the resulting polymers is shown in Table 9. The M_n (=87,000–113,000 g/mol, PDI = 1.7–2.3) of the polymers increased significantly compared to same polymers synthesized at 100 °C (Table 5).

The tensile properties also showed a significant improvement (Table 9). The UTS of PTMO-60A increased from 10 MPa to 20 MPa with 200% enhancement in the elongation at break. PTMO-80A exhibited 35 MPa UTS and 800% ultimate elongation comparable to Pellethane™ 80A. The PIB-PTMO-28-6 and PIB-PTMO-28-8 compositions showed similar improvements.

3.10. *Comparison between PIB–PTMO TPU and PTMO TPU*

A comparison of tensile properties between the PIB–PTMO based TPU and conventional TPU is listed in Table 10. According to the results PIB–PTMO based TPUs exhibit excellent mechanical properties similar to commercial Pellethane™ of the same hardness. The effect of PTMO wt% on tensile properties is depicted in Fig. 10. Depending on the hardness of the TPU these excellent properties can be reached by incorporating only 10–30 wt% PTMO in the SS.

4. Conclusions

Segmented TPUs based on PIB can be synthesized by chain extension of HO-Allyl-PIB-Allyl-OH in presence of BDO and MDI in toluene. The two-step synthetic procedure is advantageous over the one-step procedure to obtain processable polymers with high molecular weight (M_n 100,000 g/mol) and lower PDI. In spite of the much higher molecular weights than reported before the mechanical properties of resulting PIB TPUs are inferior to commercial PTMO TPUs because of possible premature phase segregation of HS and SS during synthesis as indicated from DSC analysis. TPUs exhibiting high M_n and possessing excellent mechanical properties comparable to conventional TPUs can be obtained by incorporating 10–30 wt% of PTMO diol in the soft segment. The tensile properties such as UTS and ultimate elongation of the resulting TPUs are strongly dependent on the HS:SS ratio. In a series of PIB–PTMO TPUs having similar Shore hardness, Young's modulus increases with an increase in PIB wt% in the SS. The UTS and ultimate elongation of PIB–PTMO based TPUs are comparable to PTMO based TPUs having similar Shore hardness. These TPUs can be easily processed even in the absence of conventional additives such as antioxidants and processing waxes. Further characterization and the investigation of biostability are in progress and will be reported elsewhere.

Acknowledgement

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Appendix. Supplementary information

Supporting information associated with this article may be found in the online version of this article, at doi:10.1016/j.polymer.2009.05.025.

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