Polymer 50 (2009) 3448–3457

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Syntheses and characterization of novel biostable polyisobutylene based thermoplastic polyurethanes

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ARTICLE INFO

Article history:
Received 11 March 2009
Received in revised form
23 April 2009
Accepted 14 May 2009
Available online 22 May 2009

Keywords:
Polyisobutylene
Polyurethanes
Thermoplastics

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 (≥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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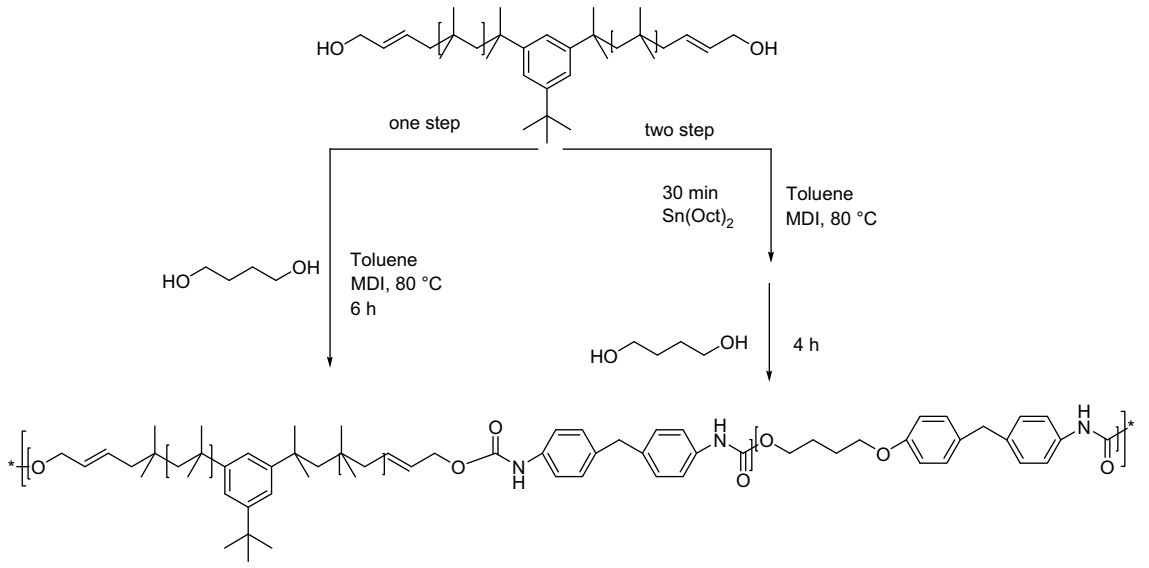
doi:10.1016/j.polymer.2009.05.025



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.