Original article

Effects of hard- and soft-segment composition on pyrolysis characteristics of MDI, BD, and PTMG-based polyurethane elastomers

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ABSTRACT

A study of the morphology changes in polyurethane elastomers (PUEs) containing different hard- and soft-segment ratios during ramped-heating pyrolysis revealed that selectivity of urethane bond cleavage is controlled by only the segment composition. Several PUEs were synthesized using 4,4′-diphenylmethane diisocyanate, 1,4-butanediol, and poly(oxytetramethylene glycol) (PTMG) to examine the influence of segment composition on pyrolysis characteristics by pyrolysis–gas chromatography/mass spectrometry, evolved gas analysis–mass spectrometry, and isoconversional kinetic studies. Soft-segment-rich PUEs tended to undergo urethane bond cleavage via a 4-membered-ring transition state, while the linkages in other compositions were selectively cleaved via a 6-membered-ring transition state. The reaction selectivity can be explained by the different conformations of the urethane bonds: in the hard-segment domains by H-bonds between urethane unit N−H and C═O groups, and in soft-segment-rich environments by H-bonds between urethane N−H groups and PTMG −O− linkages. The mechanism of PTMG pyrolysis was the same for all PUEs.

1. Introduction

As a subclass of polyurethane (PU) materials, polyurethane elastomers (PUEs) are some of the most versatile polymers due to their excellent and variable mechanical properties [1]. They are used in our daily lives in flexible tubes, films, sheets, and fibers, and as interior materials in automobiles and buildings. PUEs typically possess segmented structures consisting of alternately connected hard and soft segments. Hard segments are generally formed by PUs based on diisocyanates and short chain diols as chain extenders [1]. The soft segments are commonly formed by polyols such as polyesters and polyethers [1]. Variations in these segments provide wide degrees of tensile strengths and elasticities, and accordingly, many combinations have been developed to obtain desired properties [2–7].

Pyrolysis is a well-known technique that is used to break down polymers into smaller molecules under inert atmosphere. Most PU pyrolysis research can be classified into two categories. The first type, analytical pyrolysis, is a rapid technique that requires minimal sample quantities and no pretreatment, and can be used to reveal the original polymer structure and evaluate product quality. Identification is

generally carried out via pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS). Yoshitake et al. [8] reported that the monomeric components of the polymers can be identified by means of pattern analysis in the PU pyrograms. Ohtani et al. [9] was able to quantify the toluene diisocyanate (TDI) content in several types of PUs. Pyrolysis kinetics are generally investigated by a combination of thermogravimetric (TG) analysis and various numerical approaches [10–12]. In addition, TG has been combined with mass spectrometry (MS) and Fourier-transform infrared spectrometry (FTIR) to simultaneously analyze and identify evolved gases [13–15]. Analytical pyrolysis is helpful in the field of material science for evaluating product duration and lifetime. In the fields of the arts, archaeology, and forensic science, it is used to identify unknown polymer structures from tiny samples.

The second research category is applied pyrolysis, which is used to convert PU wastes into useful chemical feedstocks. For instance, the gasification of PU to produce syngas (H_2 + CO) has been reported [16,17], although the necessity to remove toxic hydrogen cyanide (HCN) and ammonia (NH_3) byproducts has also been described [17,18]. Terakado et al. [19] investigated the effects of metal salt additives (Zn, Cu, and Fe chlorides) on the emission of N-containing products.
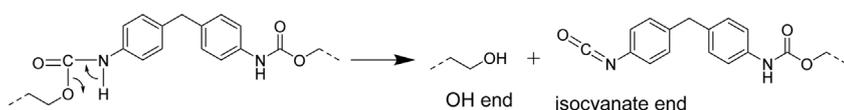
Scheme 1. Depolymerization scheme to form OH and isocyanate end groups via a four-membered-ring transition state.
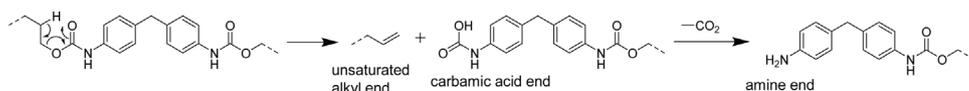
Scheme 2. Depolymerization scheme to form unsaturated alkyl and amino end groups via a six-membered-ring transition state.
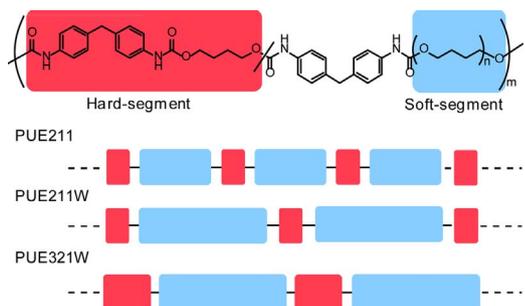

Fig. 1. Chemical structure and schematic of repeated segment structure of PUEs consisting of MDI, BD, and PTMG.

Kumagai et al. [20]. reported the almost-complete removal of HCN from the syngas stream using Ni/Mg/Al catalysts. Thus, applied pyrolysis research can facilitate proper waste management, recycling, and environmental protection practices.

Regardless of the research category, the elucidation of reaction mechanisms is important toward predicting pyrolysis behavior, pyrolysate distributions, original polymer structures, and material lifetimes. Additionally, such knowledge can enable the determination of optimum pyrolysis conditions for producing desired products. In the pyrolysis of PUEs, the hard segments (PU units) degrade first, followed by degradation of the soft segments. Two types of urethane bond cleavage mechanisms are generally accepted (Schemes 1 and 2). Scheme 1 depicts the 4-membered-ring transition state mechanism, which results in the formation of isocyanate and hydroxyl end groups, whereas Scheme 2 illustrates cleavage via a 6-membered-ring transition state to form unsaturated alkyl and carbamic acid end groups (R-NH-COO), which are further decomposed into amines and CO_2 [21]. Simon et al. [22] concluded that a Scheme 1-type scenario preferentially holds if the diisocyanate functions as an electron donor, whereas the mechanism in Scheme 2 is preferred if the diisocyanate acts as an electron acceptor. In terms of thermal stability, the nature of the polymer components also plays a role and can affect the temperature required for urethane bond cleavage. For example, PUEs based on an alkyl isocyanate/alkyl alcohol combination require higher urethane bond-cleavage temperatures, whereas the combination of an aryl isocyanate and aryl alcohol shifts that requirement lower [22]. The thermal stabilities of PUs based on poly(ethylene glycol) (PEG) and different diisocyanates such as hydrogenated 4,4′-diphenylmethane diisocyanate (H_{12}MDI), TDI, and xylene diisocyanate (XDI) were investigated, revealing the best thermal stability for H_{12}MDI [23]. In addition, MDI-based PUs are thermally more stable than the corresponding TDI-based PUs, because the absence of symmetry in TDI reduces the hard-segment crystallinity [24]. The structure of the chain extender also influences the thermal stability of PUs. Blackwell et al. [25] reported that an even number of $-CH_2-$ groups in the chain extender produces more phase-separated structure than extenders containing an odd number of carbons, which increases thermal stability. In addition, chain extenders containing side branching lead to reduced phase-separation, which decreases thermal stability [26]. It is accepted that the decomposition of soft segments proceeds via radical chain scission between C−C and C−O bonds, whereas the product distribution strongly depends on the chemical structure of the soft segment [27–31]. The thermal stabilities of PUEs

based on MDI, ethylene diamine, and different polyols such as PEG, poly(propylene glycol) (PPG), and poly(oxytetramethylene glycol) (PTMG) were investigated, resulting in the stability order PTMG-PU > PEG-PU > PPG-PU.

In summary, the effects of various combinations of diisocyanates, chain extenders, and soft segments on pyrolysis characteristics have been investigated. However, the influence of the hard- and soft-segment composition on pyrolysis characteristics such as pyrolysates distribution, pyrolysis mechanism, and kinetics is still unexplored. To the best of our knowledge, only one report has focused on these points [32], which were investigated by TG/DTA, differential scanning calorimetry, and FTIR techniques. Therefore, the dynamic pyrolysis behavior and mechanistic details remain unknown. Since PUE properties are often modified by changing the composition of hard and soft segments using the same building blocks, the elucidation of the effects of segment content on pyrolysis characteristics will be helpful for all PUE-related research.

In the present work, PUEs based on different molar ratios of MDI, 1,4-butanediol (BD) as chain extender, and PTMG as the soft segment were synthesized (Fig. 1). PUEs based on these components are well known as some of the most basic and best systems in terms of mechanical properties [3,4]. The effects of the hard- and soft-segment contents on the pyrolysis characteristics of the PUEs were investigated in detail through Py-GC/MS, evolved gas analysis-MS (EGA-MS), and isoconversional kinetic studies involving TG/DTG and model fitting.

2. Experimental sections

2.1. Materials

Two types of PTMG (with M_n = 993.11 and 1911) and the MDI having two isocyanate groups were kindly supplied by the Nippon Polyurethane Industry Co., Ltd. and Mitsui Chemicals Co., Ltd., respectively. BD was purchased from Wako Pure Chemical Industries Ltd. The BD was purified by distillation from CaH_2 under reduced pressure. Other chemicals were obtained from Kanto Chemical Co., Inc. or Tokyo Chemical Industry Co., Ltd.

2.2. Synthesis of PUEs

Three PUEs having different MDI, BD, and PTMG contents were synthesized by the one-shot method [33]. The chemical structures and segment profiles of the synthesized PUEs are shown in Fig. 1. The prepared molar ratios of the PUEs are as follows: MDI:BD:PTMG (M_n = 991.33) = 2:1:1 (PUE211), MDI:BD:PTMG (M_n = 1911) = 2:1:1 (PUE211W), and MDI:BD:PTMG (M_n = 1911) = 3:2:1 (PUE321W). The weight compositions of the hard segments of PUE211, PUE211W, and PUE321W are 25.4, 14.5, and 25.4 wt%, respectively. However, the molecular weight of the PTMG and the molar ratio of MDI and BD are different in each PUE, and therefore, the lengths of the hard and soft segments are also different. After drying the PTMG with dry nitrogen gas under reduced pressure at 100 °C for 8 h, BD was added. This mixture was mixed well with MDI at 80 °C for 20 min. An NCO INDEX ([NCO]/[OH]) of 1.01 was used, where [NCO] and [OH] are the concentrations of the NCO groups of MDI and the total OH groups of the PTMG and BD. The viscous mixture was poured into a stainless-steel