



Mass Spectrometry

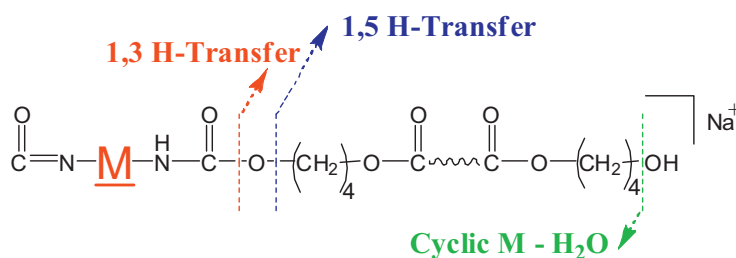
Collision induced dissociation study of ester-based polyurethane fragmentation reactions

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HIGHLIGHTS

- The first polyurethane (PUR) study using MS/MS and ion mobility separations.
- MS/MS distinguish the degree of “blockiness” within hard- and soft-block PURs.
- Ion mobility separations validated long-chain MDI hard block formation.

GRAPHICAL ABSTRACT



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ABSTRACT

A combination of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) collision induced dissociation (CID) and ion mobility separations (IMS) was used to study a complex mixture composed of unreacted polyester starting material (polybutylene adipate) and polyurethane (PUR) end products. Collision induced dissociation fragmentation identified two primary fragmentation mechanisms of PURs, which were used to generate a general fragmentation model. Predicted fragment ions were used to distinguish: (1) linear and cyclic PURs, (2) hard-block and soft-block PURs, (3) the degree of “blockiness” within hard- and soft-block PURs, (4) the location of the MDI linkages within each PUR chain, and (5) the relative intensities of various isobars intermingled within a precursor mass peak. These results were consistent with the observed IMS separations.

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1. Introduction

Polyurethanes are used widely in the coatings industry. A urethane product can be comprised of a number of ingredients, such as, isocyanates, polyols, crosslinkers, chain extenders, fillers, catalysts, and other additives [1]. For their successful application, it is of great importance to know end groups and side products present, as well as the quantity and composition of the hard and soft segments produced during synthesis [2]. These resulting polymer molecular structures can influence reactivity, processing traits, mechanical properties, and physicochemical attributes [1].

Therefore, an in-depth understanding of structure-property relationships is perhaps the most important concern for the urethane formulation chemist.

It should go without saying that a rapid (and reliable) method of polyurethane analysis would be a great help to polymer chemists. An ideal technique for generating such data is matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). However, the general problem for polymer analysis by mass spectrometry is that peaks from structurally and architecturally different species occur in the mass spectra, which can potentially be isobaric [3–8]. To overcome these challenges, tandem mass spectrometry has been investigated as a technique for distinguishing peaks from cyclic, branched, and linear species [3,9–12], as well as providing definitive identification of polymer end groups [13–16].

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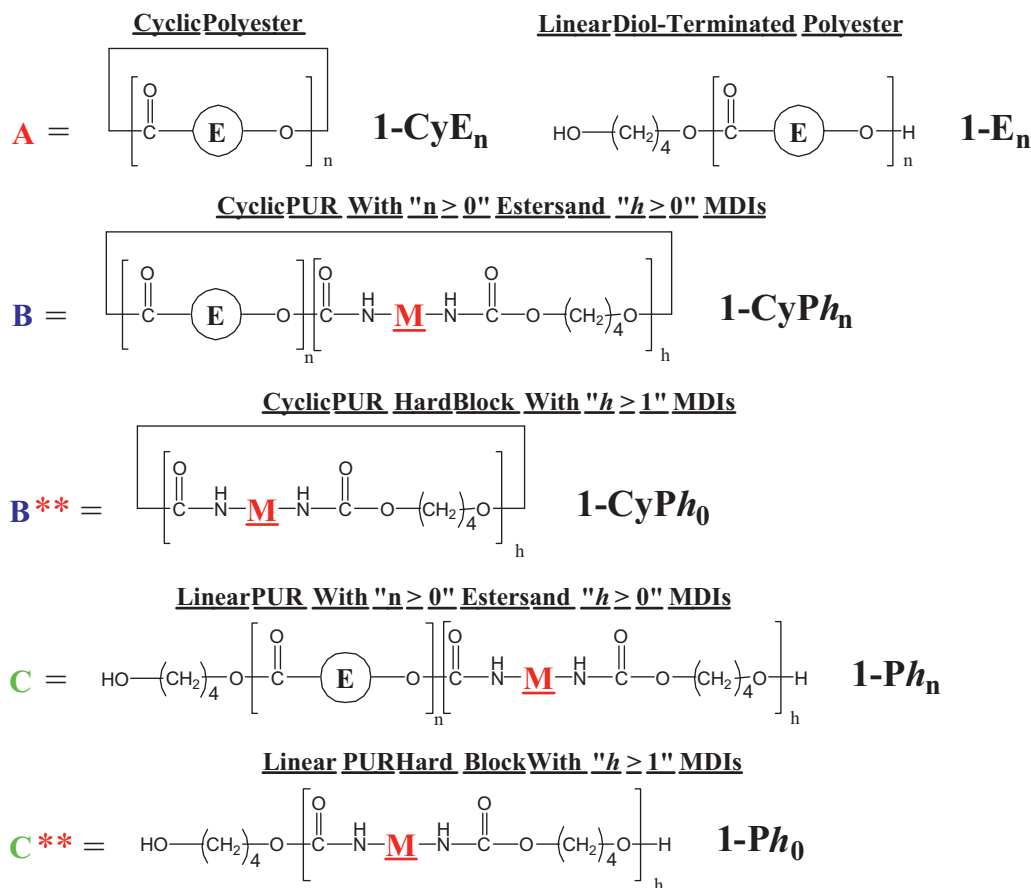
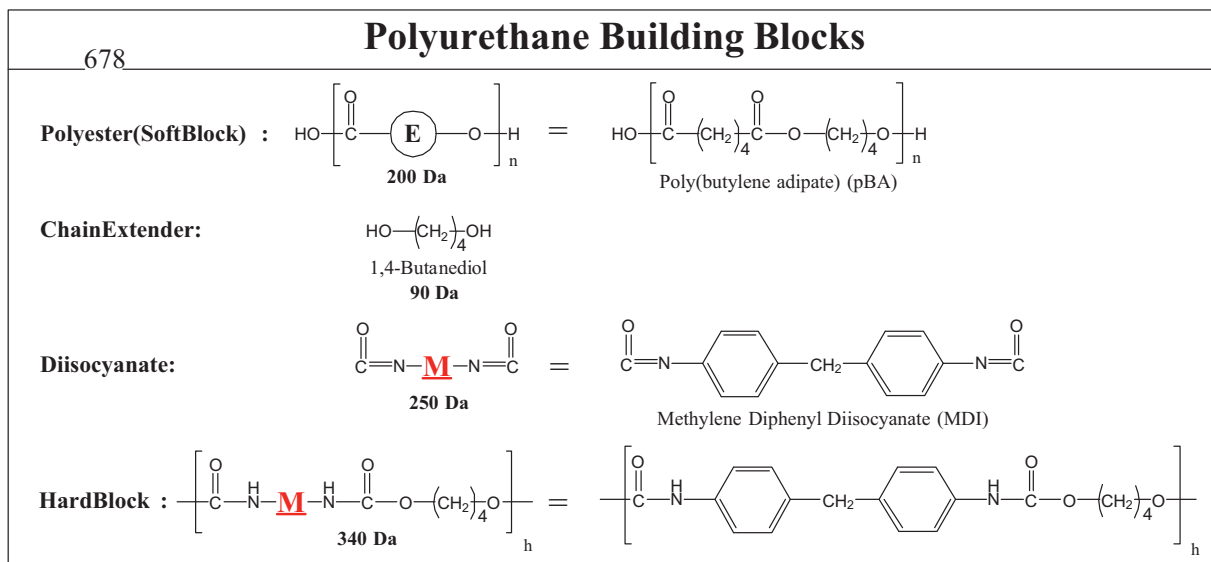


Fig. 1. Building blocks and structures of the polyurethanes synthesized from poly(butylene adipic acid) (PBA), methylene diphenyl diisocyanate (MDI), and 1,4-butanediol extender.

Our present study examined a complex mixture composed of unreacted polyester starting material (polybutylene adipate) and polyurethane end products. Collision induced dissociation (CID) fragmentation identified two primary fragmentation mechanisms of PURs, which were used to generate a general fragmentation

model. Predicted fragment ions were used to distinguish: (1) linear vs. cyclic architectures, (2) the presence of soft-blocks vs. wholly hard-block PURs, (3) the degree of “blockiness” present in a precursor ion, and (4) relative composition of isobaric species and their structural composition.

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