

## 1. INTRODUCTION

Segmented copolymers are multi-block copolymers consisting of alternating hard and soft segments along their chain backbone. The linear materials are generally synthesized via step-growth polymerization and their backbone can be represented by  $(-A-B)_n$ , where A and B are the hard and the soft components respectively. The typical degree of polymerization of the segments ranges from 10-100 and the usual polydispersity of segmented copolymers is *ca.* 2, which typically results from step-growth polymerization. In contrast, many block copolymers, for example di-(A-B) and tri-(A-B-A) block copolymers are generally synthesized via anionic polymerization, therefore allowing a narrow block polydispersity of 1.1 or less to be realized. Moreover, the degree of polymerization of the blocks is generally an order of magnitude larger than that of the segments. Nonetheless, a feature that is common to both block and segmented copolymers, which is also one of their most defining features, is the ability of these materials to develop microphase separation under appropriate conditions.

A microphase separated morphology results due to the presence of chemical incompatibility between the constituent blocks or segments. Such incompatibility may lead to macrophase separation if the blocks or segments are simply blended together. However, when copolymerized, covalent links between the constituent segments prevent macroscopic phase separation and a microphase separated morphology results instead. For diblock copolymers having no specific interactions, such as hydrogen bonding, two parameters,  $\chi N$  and  $f$ , define the phase diagram. The variable  $\chi$  is the Flory-Huggins interaction parameter,  $N$  is the overall degree of polymerization of the copolymer, and  $f$  is the volume fraction of block A or B. Under appropriate conditions for microphase separation and when the relative hard segment volume or weight fraction of the copolymer is low, they generally segregate into isolated hard microdomains that are dispersed in the continuous matrix of the soft segment phase. As the hard segment content is raised the long-range connectivity of the hard segment phase improves, which in turn is thought to promote hard phase percolation through the soft matrix. The hard domains act as physical cross-link sites and reinforce the soft matrix thereby enabling the copolymer to display useful structural properties in its 'service window'. In block/segmented copolymers this window is defined by the region of the storage

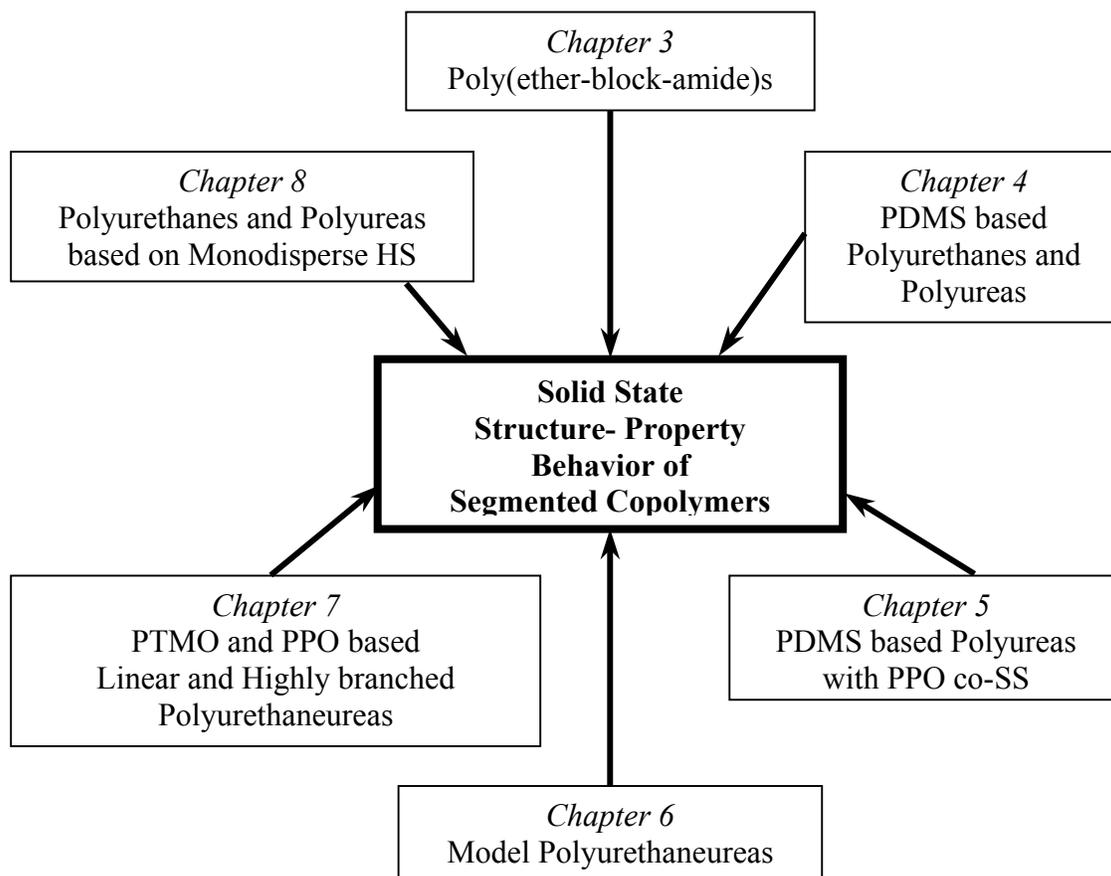
modulus,  $E'$ -temperature space where  $E'$  is relatively temperature insensitive above the soft segment  $T_g$  or  $T_m$ , if it can crystallize, and below the softening point of the copolymer's hard phase. The thermal degradation of the copolymer could become a concern well below the highest transition temperature of the hard segment and consequently may potentially limit the upper processing temperature. In addition to the copolymer's hard segment content, the extent of the hard phase percolation greatly influences the mechanical and thermal response of the material. The potential crystallizability of the hard segment and/or their ability to establish strong secondary interactions, such as hydrogen bonding, further enhance the cohesiveness of the hard domains and thereby enable the copolymer to maintain dimensional integrity under increased applied external load. The physical cross-links, unlike covalent cross-links, allow the material to be thermally reprocessed. Thus, in the absence of potentially strong hydrogen bonding (e.g. spandex), segmented copolymers are thermoplastics or thermoplastic elastomers; depending upon the relative hard and soft segment composition of the copolymer.

Segmented copolymer chemistry allows a relatively large number of variables such as backbone chemistry, segment molecular weight, the overall molecular weight of the copolymer, *etc.* to be independently controlled to engineer materials with targeted properties. The most commonly used commercial segmented thermoplastic copolymers are segmented polyurethanes, poly(etherester)s, and poly(ether-block-amide)s. Estane<sup>®</sup> (B. F. Goodrich), Hytrel<sup>®</sup> (DuPont), and PEBAX<sup>®</sup> (Atofina Chemicals) series of copolymers are examples of commercially available thermoplastic polyurethanes, poly(etherester)s, and poly(ether-block-amide)s respectively. These and related commercial materials constitute an important class of polymers that can be used to overcome some application specific limitations of conventional homopolymers or polymer blends. Components for the automotive, electronic, sporting goods, and biomedical industry, packaging, films and sheets, tubes and hoses are some of the most common applications of segmented copolymers.

Flexible water-blown polyurethaneurea foams are also 'loosely' considered to be segmented copolymers, that is, having alternating hard and soft segments along the chain backbone. However, there is an important difference between polyurethaneurea foams and thermoplastic polyurethane elastomers, namely a tri or higher functional polyol precursor is utilized during the synthesis of the former, which results in the generation of a covalent

cross-linked network. Thus, flexible polyurethaneurea foams consist of coexisting physically cross-linked and covalently cross-linked networks. The latter network prevents polyurethaneurea foams from being thermally reprocessed. The strong bidentate hydrogen bonding network within the hard segments of some linear polyurethaneureas (spandex) also has a similar consequence.

The central theme of this dissertation is the investigation of specific system variables that influence the solid-state structure-property behavior of segmented copolymers, specifically poly(ether-block-amide)s, segmented polyurethanes, polyurethaneureas, and polyureas. It is composed of six separate studies (Fig. 1.1), each of which explores a specific aspect of the structure-property behavior of these copolymers by utilizing selected material(s). Each of the six studies is addressed in a separate chapter.



**Figure 1.1** Various segmented copolymers addressed in this dissertation. Note: Acronyms utilized in this figure are provided near the beginning of the dissertation.

They follow *Chapter 2* in which a broad overview of block and segmented copolymer literature is presented. A more in-depth literature review of selected copolymers that form the basis of each of the six studies addressed in this dissertation is reserved for the appropriate chapter.

In *Chapter 3* poly(ether-block-amide) copolymers are utilized to understand how the amount of crystallinity due to the hard segment phase, soft segment molecular weight, and crystallization conditions influence the morphology and properties of these materials. A series of commercial poly(ether-block-amide) copolymers, available under the trade name PEBAX<sup>®</sup> from Atofina Chemicals, are utilized. They are based on nylon 12 as the hard segment and polytetramethylene oxide as the soft segment. The polyamide hard segment content and the ability of this component to pack into a crystalline lattice was expected to play an important role in determining the extent of microphase separation and the structure-property behavior of these copolymers. This study is published in a peer-reviewed journal [1] and the chapter's text is identical to the manuscript. However, it is modified to satisfy the formatting requirements of this dissertation. It is also to be published as part of a larger review chapter on poly(ether-block-amide)s in a handbook on thermoplastic elastomers [2].

The structure-property behavior of some unique polydimethylsiloxane based segmented polyurethanes and polyureas is presented in *Chapter 4*. Specifically, three variables - (1) soft segment MW, (2) hard segment content, and (3) chain extender type are utilized to compare polydimethylsiloxane based polyurethanes with corresponding polyureas. The question of how the stronger hydrogen bonding capability of the urea hard segment as compared to their urethane counterparts affects the solid-state structure property behavior of polydimethylsiloxane based segmented copolymers is addressed in this chapter. The results of this study are also published in a peer-reviewed journal [3] and aside from two extra figures to support the text, Chapter 3 is identical to this manuscript.

As an extension of the above research topic, a second soft segment component, specifically a polyether, is incorporated in a controlled manner along the backbone of a series of polydimethylsiloxane based polyurea copolymers. Specifically, the synthetic strategy adopted in this study enabled the positioning of the polyether segments of selected MW between the polydimethylsiloxane soft segments and the polyurea hard segments and this is the noteworthy feature of these copolymers. The effect of the specific polyether 'gradient'

component, namely, polypropylene oxide and its MW on the structure-property behavior of the resulting polydimethylsiloxane-urethaneurea copolymers is discussed in *Chapter 5*.

In continuing with the efforts to study the nature and influence of the hydrogen bonding capability of the HS in segmented polyurethanes, model oligomeric polyurethaneurea copolymers are utilized to address the question, “how important is the *extent of hydrogen bonding* in mediating the long-range connectivity of the hard phase in these materials?” This study is presented in *Chapter 6* wherein lithium chloride is utilized as a molecular probe to help elucidate the role played by hydrogen bonding. The influence of the long-range connectivity of the hard segments and the percolation of the hard phase through the soft matrix in achieving dimensional stability (solidification) is also explored. This part of the study that utilizes lithium chloride has been published in a peer-reviewed journal [4]. In the second part of this chapter, the effect of hard segment branching on the ability of the hard segments to develop long-range connectivity is addressed. A manuscript based on the results of this part of the study has been submitted to a peer-reviewed journal for publication [5]. As before, the text in Chapter 6 is identical to the above noted two manuscripts.

In *Chapter 7* the investigation of the influence of chain architecture on the structure-property behavior of segmented polyurethaneurea copolymers is presented. Specifically, segmented linear and highly branched polyurethaneurea copolymers based on polytetramethylene oxide or polypropylene oxide as the soft segments are utilized. The effect the type of soft segments on the structure/property/processing of the copolymers is investigated. The presence of intermolecular hydrogen bonding, or its absence, between different highly branched molecules is also examined by end-capping the highly branched segmented polyurethaneureas with an appropriate terminal functional group. Furthermore, the effect of the presence or absence of chain entanglements between branch points on the structure-property behavior of these materials is investigated by utilizing polypropylene oxide of MW below  $M_c$ , the characteristic MW for entanglements, or above  $M_c$ . A manuscript based on the results and text presented in Chapter 7 is being prepared for submissions to a peer-reviewed journal. However, some results of this study have already been included in a joint peer-reviewed publication [6] with Prof. T. E. Long’s group.

Finally, in *Chapter 8* non-chain extended polytetramethylene oxide based segmented polyurethane and polyurea copolymers with monodisperse hard segment length are utilized to demonstrate that proper selection of the level of hard segment symmetry and the nature of hydrogen bonding within the hard phase can enable the non-chain extended copolymers to display service window behavior comparable to chain extended systems. A manuscript based on the results and text of Chapter 8 has been submitted to a peer-reviewed journal for publication [7]. The other members of Prof. Wilkes' research group are currently undertaking a more extensive investigation of the structure-property behavior of these systems based on various diisocyanates and soft segments.