



## Amide-containing segmented copolymers



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### ARTICLE INFO

#### Article history:

Available online 28 January 2015

#### Keywords:

Segmented copolymer  
Hydrogen bonding  
Poly(amide)  
Thermoplastic elastomer  
Microphase separation

### ABSTRACT

This review highlights the synthesis, physical properties, and emerging technologies of state-of-the-art segmented copolymers containing amide hydrogen bonding sites. Amide hydrogen bonding plays a crucial role in the physical properties associated with amide-containing segmented copolymers. Amide hard segments are accessible in many different forms from amorphous alkyl amides to crystalline aramids and greatly influence copolymer morphology and mechanical properties. Variations in copolymer structure allow for the fine tuning of physical properties and the ability to predict mechanical performance based upon structural modifications. This review includes various synthetic methods for producing well-defined amide-containing segmented copolymers as well as common applications. Also, the morphological and mechanical properties associated with modifications in copolymer structure are discussed.

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**Abbreviations:** ABS, poly(acrylonitrile butadiene styrene); CLA,  $\epsilon$ -caprolactam; CLO,  $\epsilon$ -caprolactone; HMDA, hexamethylenediamide; HMDI, 4,4'-methylenebis(cyclohexyl isocyanate); HS, hard segment; PA, poly(amide); PAEI, poly(amide ester imide); PAIU, poly(amide imide urethane); PAU, poly(amide urethane); PBA, poly(butylene adipate); PDMS, poly(dimethyl siloxane); PDMS-PA, poly(dimethyl siloxane) poly(amide); PDMS-PAr, poly(dimethyl siloxane) poly(aramid); PEA, poly(ester amide); PEBA, poly(ether-*b*-amide); PEEA, poly(ether ester amide); PEG, poly(ethylene glycol); PEO, poly(ethylene oxide); PEUA, poly(ester urethane amide); PLLA, poly(L,L-lactide); PPE, poly(2,6-dimethyl-1,4-phenylene ether); PPG, poly(propylene glycol); PTMO, poly(tetramethylene oxide); PUUA, poly(urethane urea amide); ROP, ring opening polymerization; SS, soft segment; Ti(*i*-OCH<sub>3</sub>)<sub>4</sub>, titanium (IV) methoxide; Ti(OBu)<sub>4</sub>, titanium (IV) isopropoxide; TPE, thermoplastic elastomer.

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## 1. Introduction

Segmented copolymers typically consist of two covalently linked oligomeric segments with very different physical characteristics termed the hard segment (HS) and soft segment (SS). Generally, the HS and SS are molecularly incompatible with each other due to differences in the hydrophobic/hydrophilic nature of each segment. Also, strong intermolecular interactions between the HS structures, such as hydrogen bonding, lead to physical crosslinking between polymer chains [1–3]. The inherent incompatibility of the two copolymer segments in concert with physical crosslinking intermolecular interactions results in the formation of a microphase-separated morphology [4]. Factors necessary to generate a microphase-separated system include the overall degree of polymerization ( $N$ ), volume fraction of the segment ( $f$ ), and Flory–Huggins interaction parameter ( $\chi$ ) [5]. Microphase-separated morphologies consist of amorphous, semi-crystalline, or combination of both HS microdomains dispersed throughout the soft polymer matrix (Fig. 1). The extent and nature of the microphase-separated morphology, controlled through copolymer composition, significantly affects the mechanical properties of a copolymer [6].

Soft segment compositions typically include a low  $T_g$  oligomeric sequence such as poly(tetramethylene oxide) (PTMO), poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), poly(dimethyl siloxane) (PDMS), or a polyester, which impart flexibility and incompatibility with the HS [7–10]. Incorporation of polyethers into segmented copolymers serve as the soft, flexible, low  $T_g$  segment, which promotes microphase separation. Polyether SS oligomers are commercially available with varied functionality, composition, and molecular weight. These SS provide alkali and solvent resistance, varying hydrophilicity, and hydrolytic stability. However, limitations exist for polyether SS in some applications due to UV radiation sensitivity [11]. PDMS is often employed in polyamide (PA) segmented copolymers, and offers UV, thermal, and oxidative stability as well as high gas permeability, hydrophobicity, and physiological inertness [12]. PDMS is one of the most flexible polymer chains, and combined with unique physical properties, provide an excellent SS for segmented copolymers [13]. Most HS include highly polar groups, which form physical crosslinks necessary to impart microphase-separated morphologies and subsequent copolymer physical properties through intermolecular interactions such as hydrogen bonding [14]. Examples of common polar HS structures include amides [15], urethanes [16,17], ureas [18,19], imides [20,21], esters [22,23], or a combination of two or more of these functionalities [24–26]. HS structure (aromaticity, symmetry, and number of hydrogen bonding groups) and size (molecular weight, number of repeat units) play an important role in determining the physical properties of a copolymer [27,28]. Through variations in the HS architecture and subsequent intermolecular interactions, researchers effectively tuned the physical properties of many different amide-containing segmented copolymers (Fig. 2).

The amide functionality possesses strong hydrogen bonding characteristics that are well-suited for the formation of strong physical crosslinks necessary for enhanced physical properties of a segmented copolymer. When compared to other hydrogen bonding groups commonly found in segmented copolymers, amide groups impart one of the strongest intermolecular interactions. Using group contribution method calculations, the cohesive energy density of hydrogen bonding for urea, amide, urethane, and imide was 2079, 1862, 1385, and 980 J/cm<sup>3</sup>, respectively, and the hydrogen bonding energy of amide groups was 32.5 kJ/mol [29]. Primarily a result of hydrogen bond donor–acceptor sequencing within the functional group, this structural aspect becomes an important consideration when designing amide-containing segmented copolymers, and to ascertain the morphology and physical properties required for thermoplastic elastomers. Formation of PA segmented copolymers involves many different synthetic methods. Polymerization between amines and acid chlorides or carboxylic acids are efficient, often utilizing a catalyst in the case of low temperature carboxylic acid/amine polymerization [30–32]. The use of diesters and diamines are also useful for PA synthesis, but the polymerization is often inefficient due to the ester reactivity and required use of a catalyst such as an enzyme [33]. Other PA polymerization strategies include ring opening polymerization of caprolactam or polymerization between a dicarboxylic acid and diisocyanate [34]. Research continues to actively probe HS symmetry and SS composition effects on microphase-separation. As the field of amide-containing segmented copolymers grows rapidly with current research thrusts, this review discusses the various types of amide-containing segmented copolymers with emphasis on their associated synthesis, applications, and properties.

## 2. Poly(ether-*block*-amide) segmented copolymers

Poly(ether-*block*-amide) (PEBA) segmented copolymers are high performance block copolymers consisting of soft polyether blocks and hard PA blocks commercialized under the trademark Pebax<sup>®</sup>. Arkema Inc. first commercialized Pebax<sup>®</sup> thermoplastic elastomers in 1981 as part of an initiative to develop “soft” nylon materials. Development of Pebax<sup>®</sup> copolymers provided high performance materials with tunable mechanical properties. Altering the composition and length of the soft and hard blocks provides a high level of variability in copolymer physical properties [35].

Commercial applications for PEBA segmented copolymers, in particular Pebax<sup>®</sup>, include advanced gas separation membranes, biomedical devices (e.g., angioplasty balloons), food packaging, various textile modifiers (e.g., melt spun fibers), mechanical parts, construction materials, electronic equipment (e.g., wire coatings), aviation industry, and automotive applications requiring tough, elastic materials [36–40]. Pebax<sup>®</sup> possesses the ability to act as efficient gas separation membranes and the ability to alter the selectivity for a particular gas, leading to a recent increased interest in PEBA copolymers for gas separation membranes. For example, the separation of polar and nonpolar gas mixtures relied on altering the

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