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Zwitterionic, Natural Amino Acid Silicones

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PURPOSE OF THE ABSTRACT

Silicones are known for their biocompatibility and, normally, water repellency. Zwitterionic polymers have attracted interest because of their abilities to function as vehicles for gene/drug delivery, as antimicrobials, for metal chelation, antibiofouling, and as thermoplastic materials. (1) Recently several groups have shown that it is possible to create water-dispersible or soluble zwitterionic silicones by grafting betaines (2) or via the azaMichael reaction of aminosilicones with acrylic acid. (3,4) As part of a study to improve biocompatibility and to increase the content of natural materials in silicones, we report the ability to graft single or mixed amino acids onto silicones using thiol-ene and azaMichael reactions, respectively.

Random, pendent vinylsilicones are commercially available; the ability to precisely locate the vinyl groups on the backbone has been described. (5) The thiol-ene reaction of either type of starting material with cysteine led cleanly to the cysteinyl silicones that, at the upper limit of 50% substitution, are completely water-soluble (Fig. 1); at lower addition levels the materials are water-dispersible. Due to the zwitterionic end group, the cysteine-modified silicone was able to extract and chelate copper (II) ions from aqueous solution to form a gel, suggesting its use for heavy metal scavenging applications.

Acrylic-modified silicones are commercially available as simple, or more reactive, beta-hydroxyacrylate esters. (4) They are readily prepared by acrylation of hydroxy, amino, or epoxysilicones. The Michael addition with various amino acids occurred efficiently to generate amino acid-modified silicones in which the nitrogen, rather than sulfur, is the linking atom (Fig. 2A). While shown for lysine, the process is also amenable to cysteine, tyrosine, aspartic acid, and others. Lysine-modified silicone, for example, could be synthesized under near-neat conditions without any pre-treatment, and only <1 wt% water added. Telechelic lysine-functionalized silicone with molar mass from 1 - 20 kg mol-1 can be used to form crosslinked elastomers with tunable mechanical properties through secondary bonding (Fig. 2B). The resulting elastomer showed thermoplastic properties when heated at 80 °C and, at room temperature, exhibited slow self-healing over 72 hours to weeks depending on the molar mass of the silicone. The silicones with a higher amino acid content, for example, aspartic acid-modified 1000 g mol-1 telechelic silicone, were completely water-soluble and showed excellent surfactant properties and metal chelation capacity; the ability of these materials to behave as antimicrobials, antioxidants, and metal chelators is being investigated.

These simple and clean synthetic routes permit the dilution of silicone moieties with functional natural products leading to profound changes in their properties when compared to traditional silicones, particularly with respect to water compatibility.

FIGURES

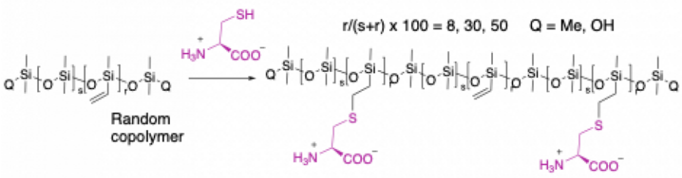

FIGURE 1

Figure 1

Thiol-ene reaction of cysteine with vinylsilicones.

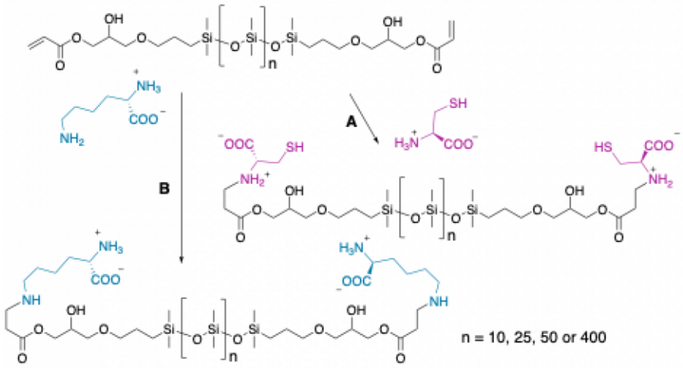

FIGURE 2

Figure 2

Aza Michael reaction of amino acides with acryloxysilicones.

KEYWORDS

Silicone | Zwitterionic polymer | Amino acids | aza-Michael

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