Progress in Polymer Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Recent developments in polypseudorotaxanes and polyrotaxanes

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ARTICLE INFO

Article history:
Received 8 July 2013
Received in revised form
18 November 2013
Accepted 21 November 2013
Available online xxx

Keywords:
Polypseudorotaxane
Polyrotaxane
Supramolecular chemistry
Interlocked molecules
Stimuli responsive materials

ABSTRACT

This review highlights developments since 2008 in the field of polypseudorotaxanes and polyrotaxanes. Progress in synthetic polyrotaxane chemistry has resulted in the preparation of numerous functionalized polymers for various applications in areas such as molecular machines, stimuli responsive materials, supramolecular gels and molecular sensors. This new genre of supramolecular polymers is advancing rapidly with several groups developing novel materials with unique characteristics.

Contents

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http://dx.doi.org/10.1016/j.progpolymsci.2013.11.005
0079-6700/

Please cite this article in press as: Arunachalam M, Gibson HW. Recent developments in polypseudorotaxanes and polyrotaxanes. Prog Polym Sci (2014), http://dx.doi.org/10.1016/j.progpolymsci.2013.11.005

1. Introduction

The synergy of non-covalent chemistry and polymer science has led to the emergence of the relatively new field of supramolecular polymer chemistry. Pseudorotaxanes are mechanically interlocked molecular architectures consisting of linear molecular components ("guests") encircled by macrocyclic components ("hosts"). Rotaxanes represent a significant family of interlocked compounds in which a dumbbell-shaped molecule is encircled by a host molecule with non-covalent interactions. As implied by their names, polypseudorotaxanes/polyrotaxanes are constructed simply by incorporating pseudorotaxane/rotaxane moieties into polymers. The development of polypseudorotaxanes and polyrotaxanes achieved great momentum in the 1990s and has defined a remarkable research area that continues to attract mounting interest among polymer and supramolecular chemists [1–9]. To date SciFinder indicates that there are 1453 citations attributed to "pseudopolyrotaxane", "polypseudorotaxane" or "polyrotaxane"; 711 (49%) of these reports appeared from 2008–2013. Here we note that "pseudopolyrotaxane" is not an appropriate term, since these species are real polymers, not "pseudopolymers"; rather, "polypseudorotaxane" is indicative of a polymer that contains pseudorotaxane units. Thus, a "polyrotaxane" is distinguished from a "polypseudorotaxane" by the presence of bulky groups in the former that prevent diffusional loss of the cyclic components. Various classes of host molecules, such as crown-ethers [4,10], cyclodextrins (CDs) [3,5,11–14], calix[n]arenes [15], cyclobis(paraquat-p-phenylene) ($CBPQT^{4+}$) [16–22] and cucurbit[n]urils (CB[*n*]) [23–32] have been explored for the fabrication of pseudorotaxanes and rotaxanes. Polypseudorotaxanes/polyrotaxanes are constructed by appropriate incorporation of pseudorotaxane/rotaxane units into polymer backbones or side chains. Recent developments in this field suggest that the proposed applications of polyrotaxanes and polypseudorotaxanes encompass a wide range of areas such as self-healing polymers, stimuli responsive materials, molecular machines, actuators and sensors. The incorporation of non-covalent interactions in the construction of polymeric architectures has an impact on the polymer-chain behavior and subsequently generates new classes of polymers with unique properties compared to covalently linked polymers. One of the striking features of non-covalent polymers over covalently bound ones is their ability to reversibly vary the degree of aggregation and relative spatial positions with respect to changes in the environmental circumstances. The quality of the research in this area, particularly in the past few years, has led to a significant advance in the understanding of the basic science behind the construction of smart functional polymeric materials. The aim of this review is to highlight advances made in the area of polypseudorotaxanes and polyrotaxanes in the years 2008 to mid-2013. However, this review should not be regarded as being comprehensive.

Below we describe efforts in the fabrication of polypseudorotaxanes and polyrotaxanes from macromolecules, conventional polymers, involving non-covalent interactions. For completeness, we should mention here that examples of supramolecular polymers have been recently reviewed [15,33–36]. However, because most of these reviews deal with supramolecular assemblies of small molecules, they will not be covered here.

Herein, recent developments in the field of polypseudorotaxanes and polyrotaxanes are reviewed in four parts as polypseudorotaxane-based stimuli-responsive materials, polypseudorotaxane-based chemosensors, organic–inorganic hybrid polyrotaxanes, and in the next section, various polypseudorotaxanes and polyrotaxanes are discussed based on their synthetic strategies.

2. Polypseudorotaxane-based stimuli-responsive materials

Non-covalent interactions enable new properties and smart functional materials by the emerging synergy between molecular recognition and polymer chemistry. Currently polyrotaxanes and polypseudorotaxanes attract much attention toward the development of self-healing smart materials. To date, several research groups have examined the fabrication of supramolecular network-like gels [37–42] from polypseudorotaxanes. An elegant demonstration of this approach is the recent work reported by Huang et al. [43], who extended the concept of pseudorotaxane assembly of dibenzo[24]crown-8 (DB24C8) with ammonium salts to deliver a supramolecular polymer in which the backbone was constructed from side chain functionalized polycrowns and bisammonium salt functionalized linker units serving as crosslinkers as shown in Fig. 1. DB24C8 has been heavily studied for its use in forming rotaxane assemblies with ammonium salts [44–48]. Mixing DB24C8 pendant poly(methyl methacrylate) (PMMA) (**1**) with two bisammonium cross-linkers linked by long flexible alkyl chains with benzyl (**2**) and cyclohexyl (**3**) end groups produced supramolecular networks **4** and **5** respectively as shown in Fig. 2. Equimolar mixtures of the **1** and **2** in chloroform/acetonitrile (v/v = 1:1) resulted in a supramolecular gel immediately. On the other hand, the supramolecular gel **5** from **1** and **3** was obtained by heating for 30 days at reflux in the same solvent system and stirring at room temperature for another 45 days; the authors cited the larger size of the cyclohexyl unit as the reason for the slow threading. ^{1}H NMR spectroscopic experiments were performed to probe the solution state complexation behavior of **1** with **2** and **3**. Due to the slow-exchange nature, the signals of each of the protons of DB24C8 and **2** split into two signals corresponding to the complexed and uncomplexed species. On the other hand,

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