



Synthesis of oligo(dimethylsiloxane)–oligothiophene alternate polymers from α,ω -dibromooligo(dimethylsiloxane)

Zhou Lu^{a,c}, Joji Ohshita^{a,*}, Daiki Tanaka^a, Tomonobu Mizumo^a, Yuki Fujita^b, Yoshihito Kunugi^{b,**}

^a Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

^b Department of Applied Chemistry, Faculty of Engineering, Tokai University, 4-1-1 Kitakaname, Hiratsuka 259-1292, Japan

^c School of Chemistry, Chemical Engineering and Environment, Qingdao University, Qingdao 266071, China

ARTICLE INFO

Article history:

Received 7 November 2012

Received in revised form

31 January 2013

Accepted 12 February 2013

Keywords:

Oligothiophene

Polysiloxane

Microphase separation

ABSTRACT

Treatment of dilithiooligothiophene with α,ω -dibromooligo(dimethylsiloxane) prepared by the Pd-catalyzed dehydrobromination of α,ω -dihydrooligo(dimethylsiloxane) with isopropyl bromide gave polymers composed of alternately arranged oligo(dimethylsiloxane) and oligothiophene units, $[(\text{Me}_2\text{SiO})_x\text{SiMe}_2(\text{C}_5\text{H}_2\text{S})_y]_n$ ($x = \text{ca. } 8, y = 2-5$). A similar reaction of α,ω -dibromooligo(dimethylsiloxane) with 5-lithio-2-bromothiophene afforded α,ω -bis(5-bromo-2-thienyl)oligo(dimethylsiloxane), which underwent the Stille coupling reaction with bis(tributylstannyl)dibutylquinquethiophene to give an oligo(dimethylsiloxane)-heptathiophene alternate polymer. Spin-coated films of the heptathiophene polymer showed semiconducting properties in the thin film transistor system after the device was annealed at 60 °C. Examination of the film morphology by AFM revealed microphase separation that affected the transistor activity.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Organopolysiloxanes are of current importance because of their unique properties, such as high thermal stability, electrical resistance, and hydrophobicity. In the course of our studies concerning the development of new synthetic routes to organohalosilanes [1], we recently found that treatment of α,ω -dihydrooligo(dimethylsiloxane) (**DMS-H2**) with allyl bromide and methyl iodide in the presence of a catalytic amount of PdCl₂ gave the corresponding α,ω -dihaloaligo(dimethylsiloxane)s, X(Me₂SiO)_xSiMe₂X (**DMS-X2**, X = Br or I), in good yields [2]. Dihalides **DMS-X2** reacted readily with a variety of nucleophiles and Lewis bases. For example, the reaction of **DMS-Br2** with 2,5-dilithiothiophene gave poly[oligo(dimethylsiloxanyl)-2,5-thienylene] (**PDMS-1T** in Scheme 1), indicating the utility of **DMS-Br2** as a macromonomer.

On the other hand, segmented copolymers composed of well-defined monodisperse π -conjugated oligomer units linked by flexible chains have found several applications as the oligomer units give rise to electronic functionality whereas the flexible chains improve the processability of the polymers. These features have underscored their potential use in electronic devices, such as

sensors and semiconducting devices [3]. Furthermore, when both the segments are adequately long, microphase separation occurs in the solid state, and this provides an opportunity to finely control film morphology that is, in turn, related to the film's functionality.

In hopes of developing new types of segmented polymers with extended π -conjugated units, we prepared alternate polymers of oligo(dimethylsiloxane) and oligothiophene units from **DMS-Br2**, in which the oligo(dimethylsiloxane) unit is anticipated to improve processability and thermal stability of the polymers. There are reports concerning the synthesis of polymeric substances bearing dimethylsiloxane-linked thiophene-based π -conjugated units [4] and silsesquioxanes prepared from the hydrolysis of bis(trialkoxysilyl)oligothiophene derivatives [5]. However, this is the first synthesis of linear segmented copolymers of oligosiloxane and monodisperse oligothiophenes that are longer than bithiophene. The semiconducting properties and microphase-separated morphology of the heptaoligothiophene derivative were also investigated in the film state.

2. Results and discussion

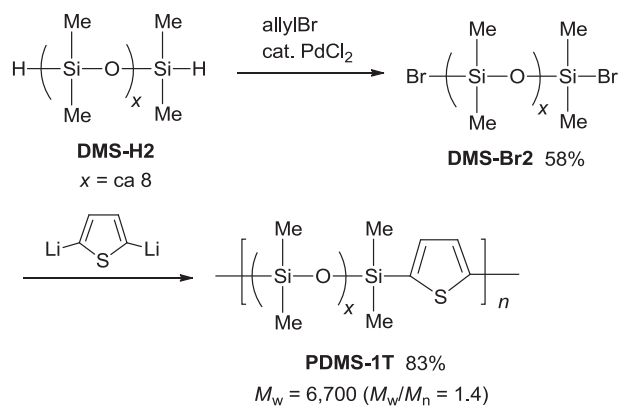
2.1. Preparation of oligo(dimethylsiloxane)–oligothiophene polymers

Recently, we reported the synthesis of α,ω -dibromooligo(dimethylsiloxane) (**DMS-Br2**) by the Pd-catalyzed dehydrobromination of

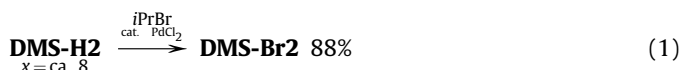
* Corresponding author. Tel.: +81 82 424 7743; fax: +81 82 424 5494.

** Corresponding author. Tel.: +81 463 58 1211x4740; fax: +81 463 50 1211.

E-mail addresses: jo@hiroshima-u.ac.jp (J. Ohshita), ykunugi@keyaki.cc.u-tokai.ac.jp (Y. Kunugi).

Scheme 1. Synthesis and polymerization of **DMS-Br2**.

α,ω -dihydrooligo(dimethylsiloxane) (**DMS-H2**, $x = \text{ca. } 8$) with allyl bromide, as shown in Scheme 1 [2]. In this study, we reinvestigated the preparation of **DMS-Br2** and found that changing the bromination reagent from allyl bromide to isopropyl bromide improved the yield from 58% to 88% (equation (1)). No changes of the siloxane chain length were observed before and after the reaction.



Oligo(dimethylsiloxane)–oligothiophene alternate polymers (**PDMS-yT**, $y = 2-5$, T = 2,5-thienylene or 3-butyl-2,5-thienylene) were obtained in a fashion similar to **PDMS-1T** [3] in 47–74% yield (Scheme 2 and Table 1). Thus, the reactions of dibromooligothiophenes (**yT-Br2**) with 2 equiv of n -butyllithium in ether ($y = 2-4$) or THF ($y = 5$) at -80°C for 3 h, followed by treatment of the resulting dilithiooligothiophenes with 1 equiv of **DMS-Br2** from -80°C to room temperature afforded corresponding copolymers, **PDMS-yT** ($y = 2-5$). The synthesis of **PDMS-5T** using ether as the solvent was unsuccessful due to the poor solubility of **5T-Br2** in ether, and it was necessary to carry out the reaction in THF. Polymers **PDMS-yT** ($y = 2-4$) were viscous oil ($y = 2$) or green yellow solids ($y = 3, 4$) and were soluble in chloroform, THF, toluene, and hexane, and partly soluble in ethanol. On the other hand, polymer **PDMS-5T** was obtained as a dark red solid that was

Table 1
Synthesis and properties of oligo(dimethylsiloxane)–oligothiophene polymers.

Polymer	Yield/%	M_w (M_w/M_n) ^a	UV λ_{max} /nm ^b	PL λ_{em} /nm ^b
PDMS-2T	59	5000 (1.6)	316	390
PDMS-3T	47	5600 (1.2)	364	429
PDMS-4T	74	3900 (1.1)	395	454
PDMS-5T ^c	64	6000 (1.2)	413	492
PDMS-7T ^c	35	15,000 (1.5)	445	559

^a Determined by GPC, relative to polystyrene standards.

^b In THF.

^c After reprecipitation.

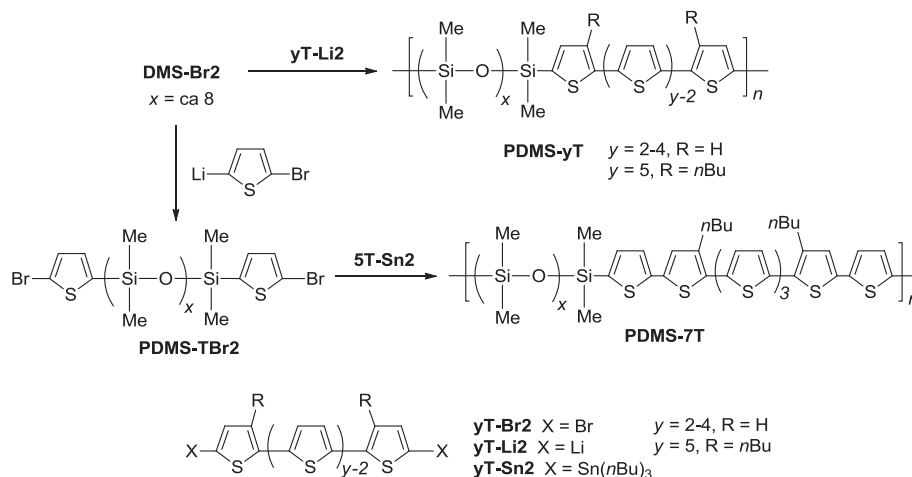
soluble in chloroform, THF, and toluene, but barely soluble in hexane, ethanol, and ether.

A polymer with a long oligothiophene segment, **PDMS-7T**, was readily prepared by the Stille cross-coupling reaction of α,ω -(5-bromo-2-thienyl)oligodimethylsiloxane (**PDMS-TBr2**) with dibutylbis(tributylstannyl)quinquethiophene (**5T-Sn2**) in 35% yield (Scheme 2 and Table 1) as a dark red solid soluble in chloroform, THF, and hot hexane, but insoluble in ethanol and ether.

The polymer structures were verified by spectrometric analysis. ¹H and ¹³C NMR spectra of the polymers were consistent with those of the regular structures shown in Scheme 2 (see Experimental section). However, the ¹³C NMR spectra of polymers **PDMS-4T** and **PDMS-5T** showed a few unidentified thiophene CH signals with low intensities, presumably ascribed to terminal thienyl and/or bromothieryl groups in the polymer chains. The molecular weights of the polymers were determined by GPC relative to polystyrene standards (Table 1). The rather small polydispersities seemed to indicate that no considerable side reactions, such as cross-linking and cleavage of the siloxane chains, competed with the polymerization, although small signals of low or high molecular weight fractions were observed in addition to the major peaks in the GPC profiles of **PDMS-3T** and **PDMS-4T**. The residual contamination of Br and Sn with atom ratios of Br/S = 0.027 and Sn/S = 0.0045 was observed by the SEM–EDX analysis of **PDMS-7T**, which corresponded to 19% and 3.1% based on an oligo(dimethylsiloxane)–oligothiophene repeating unit. No palladium contamination was detected.

2.2. Optical and thermal properties of oligo(dimethylsiloxane)–oligothiophene polymers

The optical properties of the present oligo(dimethylsiloxane)–oligothiophene polymers were investigated by measuring UV



Scheme 2. Synthesis of oligo(dimethylsiloxane)–oligothiophene polymers.

Download English Version:

<https://daneshyari.com/en/article/1321878>

Download Persian Version:

<https://daneshyari.com/article/1321878>

[Daneshyari.com](https://daneshyari.com)