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Chinese Chemical Letters 18 (2007) 758–761
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Synthesis of core–shell structured polymers with inserted thioether from a multi-functional scaffold

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Received 11 January 2007

Abstract

The synthesis of a thioether inserted, core–shell structured polymer from the scaffold of hyperbranched polyglycerol (PG) was described. PG was first allyl functionalized, and in the presence of AIBN, the allyl groups further underwent radical addition to thiol compounds, thus thiol functional polyethylene oxide monomether (MPEO) were grafted onto PG. Similarly, 2-mercaptoethylammonium chloride was introduced onto PG *via* thiol addition, and the residual amino groups were further quaternized with decyl bromide, leading to an amphiphilic core–shell structure polymer.

Keywords: Core–shell; Scaffold; Thioether; Radical addition; Hyperbranched polymer

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Hyperbranched polymers are receiving increasing interest due to their large scale and cost-effective production and interesting property, among which hyperbranched polyglycerol (PG) is a typical one [1]. Chemical modification of PG has led to a variety of core–shell structured polymers that are useful as nanocapsule [2] or nanotemplate. Thioether modified, core–shell structured PG is outstanding due to the unique affinity of thioether to various elemental/compound metal species [3–6]. Up to now, macromolecular synthesis involving thiol or thioether is still limited due to the synthetic challenge. With our continuous efforts in this field [3–7], here we describe an efficient route to synthesize thioether inserted, core–shell structured polymer based on the scaffold of PG, through this route, polyethylene oxide monomether (MPEO) or decyl can be introduced onto PG, leading to interesting core–shell structured polymer.

The first route involved in thiol functionalization of MPEO and allyl functionalization of PG (Scheme 1). Thiol functional MPEO was prepared quantitatively in one step with an efficient catalyst recently discovered by us [7], while an allyl functional $PG_{92}(allyl)_{22}$ (see ref. [8] for nomenclature), was prepared *via* *O*-alkylation of PG with allyl chloride in one step under mild condition [9]. The allyl functional PG and thiol functional MPEO underwent radical coupling in the presence of 2,2′-azobisiso-butyronitrile (AIBN), and the final product was purified by dialysis against chloroform [10]. ^{1}H NMR spectrum (Fig. 1) of the product showed that there was no longer any characteristic triplet signal of SH at 1.60 ppm, and no signal of allyl group was detected, indicating the allyl was capped by thiol groups and the unreacted MPEO was removed by dialysis.

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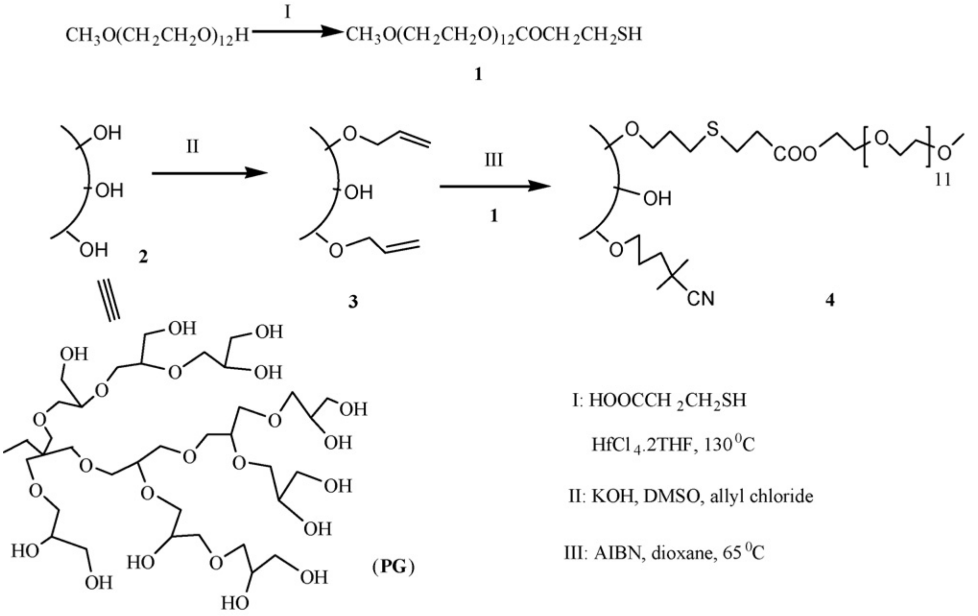
doi:10.1016/j.cclet.2007.04.005



Scheme 1. Outline of the synthesis of **4**.

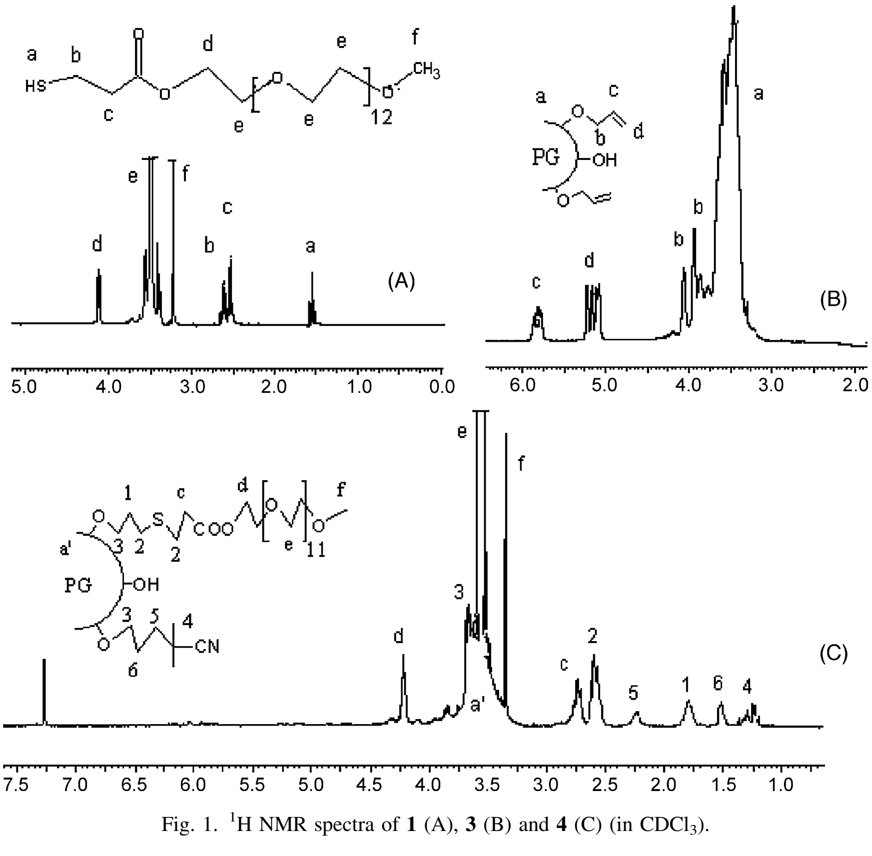


Fig. 1. ^1H NMR spectra of **1** (A), **3** (B) and **4** (C) (in $CDCl_3$).