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Gallol-containing homopolymers and block copolymers: ROMP synthesis and gelation properties by metal-coordination and oxidation

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ABSTRACT

Gallol-functionalized polymers are highly desirable for their addressable functions in the fields of materials science, nanotechnology and biomedicine, owing to gallol's unique chemistry including excellent chelating properties to metals, easily oxidability and superior ability to bind proteins. Herein, we report the controlled synthesis of the first polynorbornene-based side-chain gallol-containing homopolymers and block copolymers with pendent triethylene glycol (TEG) moieties by the ring-opening metathesis polymerization (ROMP) using the 3rd generation Grubbs catalyst **1** as the initiator. We describe the direct synthetic route by the ROMP of a gallol-containing norbornene monomer, and the indirect approach *via* an acetoxyl protection/deprotection route. Among the tested metal ions of Fe^{3+}, Mg^{2+}, Cr^{3+} and Al^{3+}, Fe^{3+} is the most effective metal ion to induce the gelation of the present gallol-containing polymers, and UV–visible spectroscopy indicates that bis-coordinated state dominates for the interaction between side-chain gallol groups and Fe^{3+} ions in DMF. The gelation rate, interior structure, thermal and mechanical properties of the Fe^{3+}-induced metallogels can be effectively tuned by changing the gallol/Fe^{3+} molar ratio, polymeric molecular weight, and by introducing of organic TEG block. Furthermore, the oxidant-induced organogels were fabricated by adding the oxidant of $NaIO_4$ into the DMF solution of the gallol-containing polymers, and the gelation rate highly depends on the gallol/IO_4^- molar ratio and the introduction of TEG block. We are convinced that the effective synthesis of well-defined gallol-containing polymers, as illustrated by the present work, will pave the way for their functional applications as smart organogels, coatings, adhesives, capsules, etc.

1. Introduction

Bio-inspired polyphenol-functionalized polymers [1], as illustrated by catechol-containing polymers [2–4], are attracting considerable attention in a wide range of research communities including materials science [5–7], analytical (bio) chemistry [8], nanotechnology [9–11] and biomedicine [12–14]. For example, 3,4-dihydroxyphenylalanine (Dopa), found in mussel foot proteins (Mfps) that are known to cure rapidly to form adhesive plaques with high interfacial binding strength, durability, and toughness [15], has been elegantly tethered to natural (chitosan [16–18], hyaluronic acid [19], alginate [20], gelatin [21], collagen [22], polypeptide [23], etc.) and synthetic (poly(ethylene glycol) [24–26], polyacrylamide [27–29], polystyrene [30–32], polyacrylate [33], polyallylamine [34], polyurethane [35], poly(-phosphoester) [36], poly(ester urea) [37], etc.) polymer backbones as a unique and versatile platform to develop underwater/biomedical adhesives [38–43], self-healing hydrogels [44–46], drug carrier for cancer therapy [47–49], hemostatic materials [50], biosensors [51], antifouling coatings [52], and so on. Indeed, the *o*-dihydroxybenzene structure of catechol-functionalized polymers permits its involvement in many molecular interactions including hydrogen bonding, metal coordination, π-π electron interaction, cation–π interaction and oxidation-mediate covalent crosslinking under mildly basic conditions [4,6,7].

Recently, researchers have looked to another plant-derived polyphenol-containing polymer, namely, gallol-functionalized polymer due to its fascinating pyrogallol structure and

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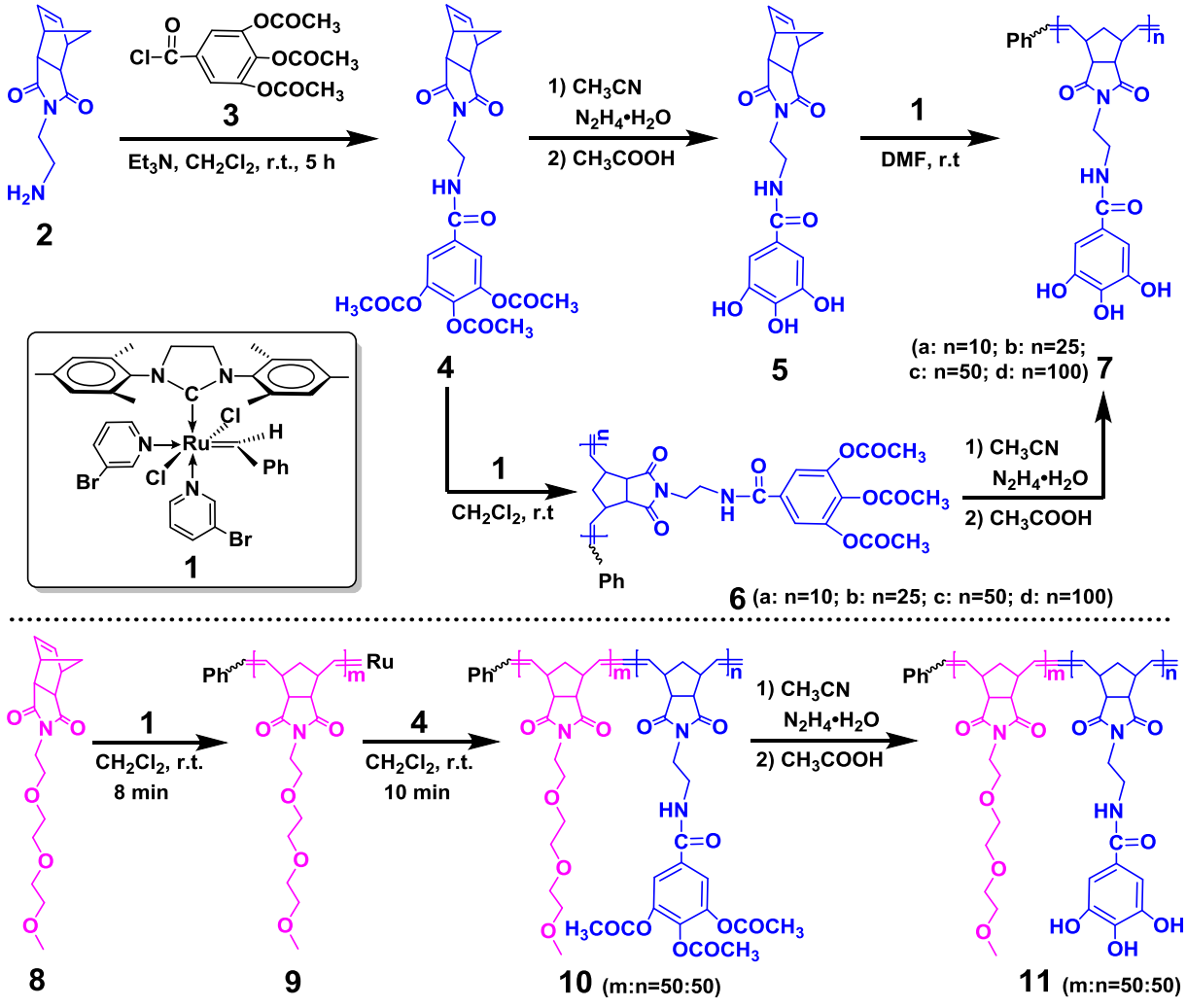
multifunctionality [53]. Gallol has a unique chemical structure of three adjacent hydroxyls attached to benzene, and exhibits robuster interactions than catechol with biomacromolecules (peptides, proteins, DNA or RNA) [54,55] and metal ions [53] *via* hydrogen bonds, hydrophobic interactions, metal coordination interaction, π-π interaction [56–58] and auto-oxidative covalent crosslinking [59,60]. Based on this, various multifunctional materials including smart hydrogels [61–63], coatings [64–66] and capsules [67–70] were fabricated by using a natural gallol-containing macromolecule, namely, tannic acid (TA), an extract of plant materials such as Chinese gallnuts, cacao, green tea leaves, and fruit peels. However, one of the major disadvantages for TA is its impurity as plant extracts with little control over the size or chemical structure [71]. It is challenging and highly desirable to prepare well-defined gallol-containing polymers with various topological structures. For example, Shin and Lee [54] prepared the gallol-functionalized hyaluronic acid (HA-Ga) by a 1-ethyl-3-(3-(dimethylamino)propyl) carbodiimide (EDC)/N-hydroxysuccinimide (NHS) coupling reaction using 5-hydroxydopamine, and the corresponding hydrogels by mixing HA-Ga with oligo-epigallocatechin gallate (OEGCG). The gallol moieties were demonstrated to be crucial for easily achieving shear-thinning, injectable protein-encapsulated hydrogels showing enzymatic resistance for biomedical applications. Ejima and Yoshie et al. [72] reported the controlled synthesis of a TA-inspired gallol-functionalized polymer, polyvinylgallol (PVGal), by using the reversible addition-fragmentation chain transfer polymerization (RAFT). A methoxy protection/deprotection route was adopted, and the obtained PVGal exhibited greater antioxidant and absorption activities than the widely used catechol-functionalized polymers. Recently, the same group [73] also synthesized PVGal-based copolymers as underwater adhesive *via* the methoxymethyl protection/deprotection route. The prepared gallol-containing copolymers showed stronger adhesive performances (typically 7 × stronger in water) than the widely used catechol-functionalized copolymers under all tested conditions (in air, water, seawater, or phosphate-buffered saline solution), which is attributed to the tridentate-related interfacial interaction and chemical crosslinking [73]. Even so, research in this filed is only in its infancy, and until now, there are only a few reports related to the synthesis and functional applications of gallol-functionalized polymers [54,56–60,71–74].

Herein, we report the synthesis of novel gallol-containing homopolymers and block copolymers through the living and controlled ring-opening metathesis polymerization (ROMP) technique with the aid of Grubbs' very efficient third generation ruthenium-benzylidene catalyst **1** having highly functional group tolerance [75–77]. This work describes two new synthetic routes (Scheme 1), namely, the direct ROMP of a gallol-containing norbornene monomer **5**, and the indirect method that includes the



Scheme 1. ROMP synthetic routes of gallol-containing homopolymers and block copolymers.