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Note

The synthesis and ring-opening metathesis polymerization of an amphiphilic redox-active norbornene

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Abstract

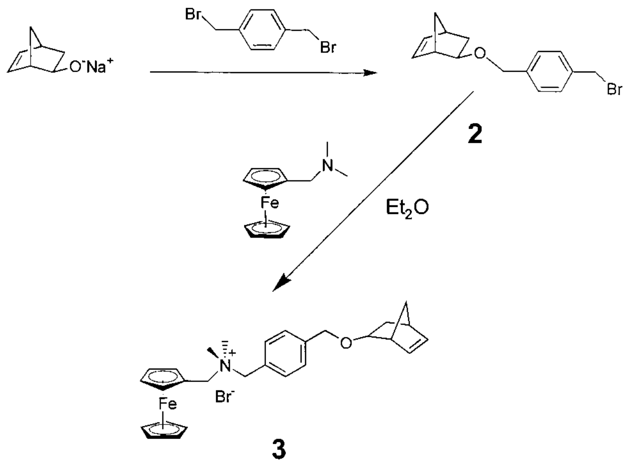
The synthesis and characterization of an amphiphilic, ferrocenyl-modified norbornene is reported. Linked together through a quaternary ammonium salt, the norbornenyl moiety makes this monomer susceptible to ring-opening metathesis polymerization (ROMP) using $(PCy_3)_2RuCl_2$=CHPh, while the ferrocenyl group allows for the incorporation of a redox-active group in the polymer backbone. The resulting polymers are soluble in both aqueous and organic media. Such polymers are important for the development of materials for electrochemically-based diagnostic applications. Cyclic voltammetry studies revealed that reversible redox waves are observed for both the monomer and polymer, although the $E_{1/2}$ of the polymer is approximately 145 mV lower than that of the monomer, reflecting very different local environments. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polymer; Norbornene; Ferrocene; Metathesis; Quaternary ammonium salt

1. Introduction

The development of polymers which contain transition metals (TMC-polymers) is an area that has received a great deal of attention in recent years [1]. In addition to providing insight into important fundamental electron transfer problems, these materials are being evaluated for their use in the development of magnetic [2], electronic [3], and diagnostic [4] devices. In the case of diagnostic applications, many of these materials need to be water soluble, especially when biological molecules are the targets of interest. When incorporated into a detection scheme, these TMC-polymers can give rise to large, detectable signals that are based on their intrinsic electrochemical, fluorescent, or magnetic properties [4].

Recently, we reported the surface modification of organic-soluble gold nanoparticles with TMC-block copolymers containing two different ferrocenyl moieties [5]. In this approach, we used the ruthenium catalyst $(PCy_3)_2RuCl_2$=CHPh (**1**) [6] to initiate the surface-confined ring-opening metathesis polymerization (ROMP) reaction [7]. The resulting core shell materials



Scheme 1.

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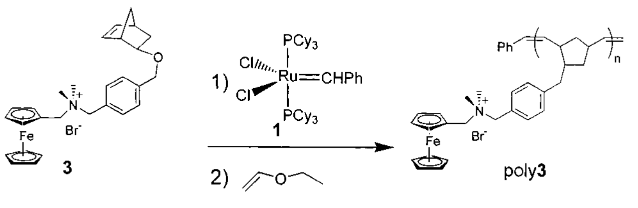

Scheme 2.

can be synthetically tailored with regard to polymer shell thickness, composition, and function and have the potential to be used in the fabrication of a wide array of electronic and diagnostic devices.

In order to utilize TMC-ROMP-generated polymers and core-shell nanoparticle-based materials for biological applications, it is essential that they be designed to be water-soluble. Two approaches can be taken to achieve this goal. (1) Water-soluble monomers can be polymerized in aqueous media using a water-soluble and water-compatible ROMP catalyst, or (2) amphiphilic monomers can be polymerized in organic media and then redispersed in aqueous solution. Herein, we report a strategy based on the latter approach, which utilizes a novel amphiphilic ROMP-active ferrocene to prepare water soluble, redox-active metallocene containing polymers [8]. The synthesis and characterization of the metallocene-containing monomer and polymer are described.

2. Results and discussion

2.1. Monomer synthesis

Our strategy for the synthesis of **3** consists of three steps, as outlined in Scheme 1. First, a readily available norbornene starting material with a nucleophillic functionality, *exo*-5-norbornene-2-ol, was prepared and isolated using literature procedures [9]. The *exo*-isomer was chosen to maximize ROMP activity [10]. Next, the alcohol was coupled to a di-functional electrophile, α,α′-dibromo-*p*-xylene, to afford the monobromide **2** in over 50% yield. Purification of **2** from unreacted starting material and the doubly substituted product was readily accomplished using column chromatography on silica. Finally, the reactive bromide moiety of **2** was displaced by the amine group of (*N*,*N*-dimethylaminomethyl)ferrocene, affording **3** in high yield (> 70%). The resulting quaternary ammonium salt bridge not only connects the ferrocenyl moiety to the norbornenyl group, but also provides the charge necessary to make **3** a water-soluble monomer.

Aside from its high solubility in water, **3** also was found to be soluble in many polar and non-polar organic solvents, including acetone, MeOH, $CHCl_3$, CH_2Cl_2, DMF, DMSO, benzene, and toluene. Like many quaternary amines, **3** is quite hygroscopic and will form an aqueous solution if left under normal atmospheric conditions for long periods of time (~ 3 h) [11].

2.2. Ring-opening metathesis polymerization of 3

An initial survey of the ROMP-activity of **3** in various solvents was carried out using catalyst **1** (Scheme 2). In these experiments, **3** was dissolved in the desired solvent and mixed with a catalytic amount of **1**. The reactions were monitored by ^{1}H-NMR spectroscopy and, in some cases, by visual inspection of the formation of a solid polymeric precipitate. The solubility of the polymer does not mirror that of the monomer; indeed, the propagating polymer precipitates before 100% conversion from all but the most polar organic solvents, such as DMF-d_7 and $CD_3OD/CDCl_3$ (8:1 mixture). This result is consistent with previous literature reports of polymers containing quaternary amines, which also exhibit lower solubilities than their monomer precursors [11]. The polymer's solubility, as compared with that of the monomer, is dramatically reduced in such solvents as CH_2Cl_2, $CHCl_3$, C_6H_6, and 1,2-dichlorobenzene [11]. The resulting polymer can be isolated by first terminating the reaction with ethyl vinyl ether [12], and then pouring the reaction mixture into diethyl ether. The sticky, yellow polymer product can be redissolved in DMF, MeOH, or water.

In $CD_3OD/CDCl_3$ (8:1), the polymerization of **3** was found to be complete in less than 30 min. In DMF-d_7, however, the polymerization was slowed by the coordinating properties of the solvent, which allowed for a careful examination of the polymerization reaction by ^{1}H-NMR spectroscopy. Five minutes after mixing **3** and **1** together in DMF-d_7, the ^{1}H-NMR spectrum of the reaction mixture revealed that the catalyst was completely initiated (as signaled by the loss of the starting singlet carbene resonance at 20.11 ppm, and the subsequent formation of two multiplets in a 2:1 ratio representing the initiated catalyst). Significantly, the olefinic resonances of the monomer at 5.9 and 6.2 ppm are only reduced by an amount which compares well with the amount of catalyst used, implying that monomer initiation is faster than polymer propagation. An overall view of the polymerization reaction is summarized in Fig. 1, which highlights the olefinic region of the ^{1}H-NMR spectrum of this reaction after 1, 4, and 7 h. After 1 h, the reduction in the olefinic resonances of the norbornene starting material at 5.9 and 6.2 ppm is significant, but the polymerization is not complete. However, the growth of new resonances associated with polymer in the 5.2–5.5 ppm region is now quite distinct. After 4 h, the resonances at 5.9 and 6.2 ppm are almost completely reduced to the baseline. Finally, after 7 h of reaction time, the resonances at 5.9 and 6.2 ppm are no longer detectable, signaling the complete consumption of the monomer.

To further elucidate the physical properties of poly**3**, a larger scale polymerization (> 100 mg) was carried out in 8:1 MeOH:CHCl$_3$. Because of the differences in polymerization rate in this solvent mixture as compared to DMF (vide supra), end-group analysis of the resulting purified polymer was performed to obtain the number-average molecular weight [13]. Integration of the olefinic peaks associated with the end-group in the ^{1}H-NMR spectra of the polymer (compared to the interior olefinic resonances) revealed that the degree of polymerization (DP) was 24, which compares well to the theoretical value of 25 (for a monodispersed polymerization). Furthermore, this DP agrees with the NMR analysis of the polymerization in DMF-d_7, described above, where the rate of initiation appears to be much faster than the rate of propagation. Thus, even though the overall polymerization rate in 8:1 MeOH:CHCl$_3$ is faster than that in DMF-d_7, the resulting polymers should be similar in the overall molecular weight dispersity.

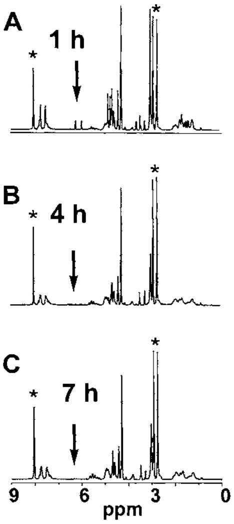

Fig. 1. ^{1}H-NMR spectra of the polymerization of **3** using **1** in DMF-d_7 after (A) 1 h; (B) 4 h, and (C) 7 h (asterisk = solvent peaks, arrow highlights olefinic region).

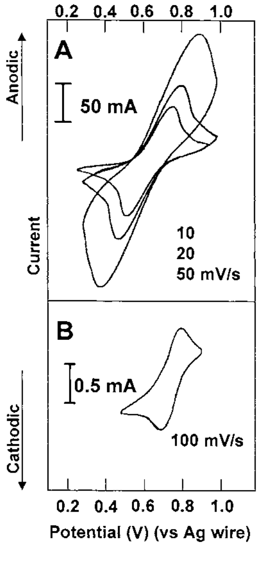

Fig. 2. Cyclic voltammetry of (A) poly**3** (film cast onto 0.4 cm$_2$ Au electrode, 0.1 M TBAPF$_6$) and (B) **3** in CH$_2$Cl$_2$.

2.3. *Cyclic voltammetry of **3** and poly**3***

The cyclic voltammetry of **3** in 0.1 M n-Bu$_4$NPF$_6$ in MeOH exhibits a reversible wave with an $E_{1/2}$ of 645 mV (vs. Ag wire). However, when poly**3** was dissolved in a fresh solution of 0.1 M n-Bu$_4$NPF$_6$ in MeOH, an anion exchange reaction took place between Br$^-$ and the PF$_6^-$ of the electrolyte, causing the polymer to precipitate from solution. To circumvent this precipitation problem, poly**3** was cast onto a gold electrode and studied by cyclic voltammetry in 0.1 M n-Bu$_4$NPF$_6$/CH$_2$Cl$_2$, an electrolyte that does not dissolve the polymer, Fig. 2A. The homogeneous voltammetry of **3** in 0.1 M n-Bu$_4$NPF$_6$/CH$_2$Cl$_2$ was taken for comparison purposes, Fig. 2B. Reversible redox waves are observed for both systems, although the $E_{1/2}$ of the polymer is ca. 145 mV lower than that of the monomer, reflecting very different local environments. In addition, the surface-confined polymer exhibits broader waves with non-ideal peak-to-peak separations (substantially greater than 0), characteristic of sluggish ion transport through the polymeric film.

3. Experimental

3.1. *General considerations*

All reactions were carried out under a dry nitrogen atmosphere using either standard Schlenk techniques or in an inert-atmosphere glovebox unless otherwise noted. Tetrahydrofuran (THF) and diethyl ether were distilled over sodium–benzophenone. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification, except for CDCl$_3$ and CH$_2$Cl$_2$, which were distilled over calcium hydride and vacuum transferred into air-tight solvent bulbs prior to transfer into the inert-atmosphere glovebox. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini 300 FT-NMR spectrometer (300 MHz for ^{1}H-NMR, 75 MHz for ^{13}C-NMR). ^{1}H-NMR data are reported as follows: chemical shift (multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and assignment). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the residual solvent resonances as internal standards.

Cyclic voltammetry was performed on either a Pine AFRDE4 or Pine AFRDE5 bipotentiostat with either a Kipp en Zonen BD90 X-Y or a Linseis LY 1400 recorder. A conventional three-electrode cell was used for all electrochemical experiments (Au/Si working electrode, Ag wire reference electrode, and Pt gauze counter electrode). All flash column chromatography was carried out using a 56 mm inner-diameter column containing 200 mm (length) of silica gel under a positive pressure of nitrogen, unless otherwise noted.

3.2. Materials

The Ru catalyst **1** [6] and *exo*-5-norbornene-2-ol [9] were prepared using literature methods. All other chemicals were purchased from the Aldrich and used without further purification, except for (*N*,*N*-dimethylaminomethyl)ferrocene, which was purchased from Lancaster Synthesis.

3.3. Synthesis of α-bromo-α′-(exo-5-norbornene-2-ol)-p-xylene (2)

In an inert atmosphere glovebox, *exo*-5-norbornene-2-ol [9] (820 mg, 7.44 mmol) was weighed into a 50 ml Schlenk flask. Dry THF (15 ml) was added and the solution was stirred vigorously while oil-free sodium metal (250 mg, 10.9 mmol) was added. The mixture was then taken out of the glovebox, refluxed for 12 h under a positive stream of nitrogen, and allowed to cool to room temperature (r.t.). In a separate 100 ml Schlenk flask, α,α′-dibromo-*p*-xylene (2.11 g, 8.00 mmol) was dissolved in dry THF (15 ml), and the flask was capped with a pressure-equalizing dropping funnel. The cooled solution of deprotonated *exo*-5-norbornen-2-ol was then transferred to the pressure-equalizing dropping funnel using a cannula needle and slowly added to the xylene solution with vigorous stirring over a period of 10 min. The dropping funnel was then replaced with a condenser and the mixture was refluxed for an additional 12 h under a positive stream of nitrogen. Upon cooling to r.t., the reaction mixture was poured into benzene (50 ml) and washed successively with water (50 ml), 1.0 M NaOH (50 ml), 1.0 M HCl (50 ml), and brine (50 ml). The organic layer was collected, dried over sodium sulfate, and filtered into a 500 ml round bottom flask. The solvent was removed using a rotary evaporator. Column chromatography on silica gel with 30% CH_2Cl_2 in hexanes as the eluent gave the desired product **2** (1.13 g, 3.87 mmol, 52%) as a clear oil. ^{1}H-NMR (C_6D_6): 1.42–1.85 (mm, 4H, 3- and 7-norbornenyl-*H*s), 2.61 (m, 1H, 1-norbornenyl-*H*), 2.84 (m, 1H, 4-norbornenyl-*H*), 3.44 (m, 1H, 2-norbornenyl-*H*), 3.99 (m, 2H, C*H*$_2$–Br), 4.24 (m, 2H, C*H*$_2$–O), 5.76 (m, 1H, 6-norbornenyl-*H*), 6.01 (m, 1H, 5-norbornenyl-*H*), 7.02 (m, 2H, Aryl–*H*s), 7.13 (m, 2H, Aryl–*H*s). ^{13}C-NMR (C_6D_6): 33.6 (*C*H$_2$–Br), 35.2 (3-norbornenyl-*C*), 41.2 (4-norbornenyl-*C*), 46.7 (7-norbornenyl-*C*), 47.2 (1-norbornenyl-*C*), 71.1 (*C*H$_2$–O), 80.7 (2-norbornenyl-*C*), 129.6 (Aryl–*C*), 133.7 (6-norbornenyl-*C*), 137.5 (Aryl–*C*), 140.3 (Aryl–*C*), 141.2 (5-norbornenyl-*C*). HRMS(EI): Calc. for $C_{15}H_{17}BrO$: 292.0463. Found: 292.0462.

3.4. Synthesis of N,N-dimethyl-N-(1-ferrocenylmethane)-N-[α-(α′-exo-5-norbornene-2-oxy)-p-xylene ammonium bromide (3)

Into a 100 ml round bottom flask was added **2** (293 mg, 1.00 mmol), anhydrous diethyl ether (25 ml) and a magnetic stirring bar. To this stirring solution was added a solution of (*N*,*N*-dimethylaminomethyl)-ferrocene (243 mg, 1.00 mmol) in anhydrous diethyl ether (25 ml). The mixture was stirred for 6 h, during which time a yellow precipitate formed. The ether mother liquor was then removed from the flask via cannula filtration and the resulting yellow powder was washed with ether (4 × 50 ml). The remaining solid was dried overnight under vacuum to yield the desired product **3** (391 mg, 0.73 mmol, 73%). ^{1}H-NMR (D_2O): 1.31–1.66 (mm, 4H, 3- and 7-norbornenyl-*H*s), 2.80 (b, 7H, (C*H*$_3$)$_2$N and 1-norbornenyl-*H*), 2.95 (m, 1H, 4-norbornenyl-*H*), 3.70 (m, 1H, 2-norbornenyl-*H*), 4.28 (m, 5H, Cp-*H*s), 4.37 (b, 2H, Cp–C*H*$_2$–N$^+$), 4.45 (m, 2H, Cp-*H*s), 4.46 (b, 2H, Aryl–C*H*$_2$–N$^+$), 4.53 (m, 2H, Cp-*H*s), 4.62 (m, 2H, C*H*$_2$–O), 5.95 (m, 1H, 5-norbornenyl-*H*), 6.23 (m, 1H, 6-norbornenyl-*H*), 7.49 (b, 4H, Aryl–*H*s). ^{13}C-NMR ($CDCl_3$): 34.7 (Aryl–*C*H$_2$–N$^+$), 40.6 (3-norbornenyl-*C*), 46.2 (4-norbornenyl-*C*), 46.7 (7-norbornenyl-*C*), 48.3 (1-norbornenyl-*C*), 65.8 (*C*H$_2$–O), 66.9 (Cp–*C*H$_2$), 69.8 (N(*C*H$_3$)$_2$), 70.7 (Cp–*C*), 70.8 (Cp–*C*), 72.5 (Cp–*C*), 80.9 (2-norbornenyl-*H*), 126.7 (Aryl–*C*), 128.3 (Aryl–*C*), 133.2 (6-norbornenyl-*C*), 133.5 (Aryl–*C*), 141.0 (Aryl–*C*), 142.0 (5-norbornenyl-*C*). MS(APCI): Calc. for $C_{28}H_{34}FeNO^+$: 456.1990. Found: 456.1997.

3.5. General polymerization procedure

In an inert atmosphere glovebox, **3** (110 mg, 0.21 mmol) was weighed into a 25 ml round bottom flask equipped with a magnetic stirring bar. Dry MeOH (4 ml) was added, followed by a solution of catalyst **1** (7.0 mg, 0.0085 mmol, 4 mol%) in dry CH_2Cl_2 (0.5 ml). The mixture was stirred for 30 min, after which time it was removed from the dry box and the polymerization was terminated with ethyl vinyl ether (1 ml). The polymer (ROMP-poly**3**, 101 mg, 92%) was isolated by pouring the mixture into anhydrous diethyl ether (100 ml), filtering, and repeatedly washing with fresh diethyl ether (4 × 50 ml).

4. Conclusions

To summarize, we have reported a novel amphiphilic ROMP monomer that incorporates a water soluble ammonium salt, ROMP-capable norbornenyl group, and a redox-active ferrocenyl moiety. The solubility of monomer **3** in a wide range of solvents allows for the polymerization to be conducted using the commercially available, organic-soluble catalyst **1**. Poly-**3** is soluble in both polar organic solvents (such as DMF and MeOH) and in water, circumventing the problems associated with the synthesis of polymers in the aqueous phase (i.e. emulsion polymerization) and/or the need for aqueous compatible catalysts. Importantly, our strategy can be extended to include many other molecules, which contain a ammonium functionalities, opening up new avenues to polymers with structurally programmable parameters.

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