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Synthesis of an A/B/C Triblock Copolymer for Battery Materials Applications

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ABSTRACT: An A/B/C triblock copolymer has been synthesized having potential applications as a self-contained nanoscale battery. A new organometallic compound was synthesized which serves as the anode. The polyelectrolyte block of the copolymer is an unsaturated polyether. The last block acts as the template to form metal oxide clusters and functions as the cathode. The triblock copolymer was synthesized by ring-opening metathesis polymerization using Grubbs's catalyst. GPC and NMR were used to monitor the polymerization. ^{1}H and ^{13}C NMR, FTIR, UV−vis, GPC with light scattering, and XPS were used to characterize the synthesized polymer.

Introduction

The synthesis of a novel polymeric nanocomposite is presented with potential application in battery materials. Polymeric materials are processed as sheets and films and can be molded to a variety of shapes; thus, flexible batteries could be designed on the basis of this concept. The active material used in this investigation is an A/B/C triblock copolymer where the constituent blocks comprise the anode, electrolyte, and cathode. The anode block consists of an organocobalt block, the electrolyte block is a poly(ethylene oxide) analogue, and the cathode block has polar functionalities that can incorporate metal salts. The organocobalt monomer was chosen due to the difficulty of polymerizing a lithium-containing monomer. The electrochemical reaction shown in reaction 1 is different from other lithium battery systems where the reduction of lithium oxide occurs.[1,2] A monomer containing lithium would have deactivated the Grubbs catalyst, whereas a monomer containing a transition metal has been polymerized before.[3] In addition, an organometallic anode monomer is required, for one of the blocks of the A/B/C triblock, because there is no mechanism to cause preferential metal coordination for each anode and cathode block.

$$CoO + 2Li^+ + 2e^- \leftrightarrows Co + Li_2O \qquad (1)$$

Anode materials that serve as lithium hosts are common, such as the SnLi alloys.[4,5] The cobalt system was more amenable to polymerization, and the facile synthesis of cobalt oxide from the polymer aids in processing. All monomers and polymers were characterized with ^{1}H NMR to determine chemical structure. GPC was performed to determine polymer properties. Ion conduction in the A/B/C triblock battery system is achieved with a ROMP polyether[14] as the middle block. The structure of this polyether closely resembles poly(ethylene oxide), which is often used as the ion conducting polymer in battery systems.[11,12] The cathode block of the battery is a poly(norbornene−dicarboxylic acid), which serves as a template for the synthesis of metal oxide nanoparticles.[6−10]

A lithium ion battery configuration was chosen as the candidate system due to the high power density of lithium. The metal oxides serving as the cathode in this system can be $LiMn_2O_4$ or $LiCoO_2$, depending on the desired cathode. This work deals primarily with characterizing the synthesis of the A/B/C organometallic triblock copolymer. The cobalt block was polymerized first, followed by the electrolyte and the cathode block. A synthetic scheme for the triblock is depicted in Figure 1.

Experimental Section

tert-Butylamine, cobalt chloride, and ethyl vinyl ether were purchased from Aldrich. Butyllithium (2.5 M in hexane) was purchased from Acros Organics. Grubbs's catalyst, 1,3-bis(tricyclohexylphosphino)[benzylidene]ruthenium dichloride, and tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidine]ruthenium(IV) dichloride (Grubbs's second generation catalyst) were purchased from Strem Chemicals. Anhydrous tetrahydrofuran (THF), diethyl ether, benzene, and pentane were purchased from Fisher. THF, benzene, and diethyl ether were distilled over sodium benzophenone ketyl under argon and stored in the glovebox. Pentane was washed with a mixture of 5% nitric acid and sulfuric acid, stored over calcium chloride, and then distilled over sodium benzophenone ketyl under argon. All syntheses were performed under argon unless otherwise noted.

The starting monomers for the anode were 5-norbornene-2,3-di-*tert*-butylamine. The monomer was prepared according to literature procedures.[3] The monomer was converted to an organometallic monomer via lithiation[3] with butyllithium and exchange with cobalt chloride. Treatment with cobalt chloride affords 5-norbornene-2,3-di-*tert*-aminocobalt (Co(bTAN)). The second monomer is a ring-closed metathesis product of allyl end-capped triethylene glycol, tetraoxacyclotetradecene (TOCD). The third monomer is norbornenedicarboxylic acid trimethylsilyl ester (NORCOOTMS).

This triblock polymer consists of an norbornene−diamido cobalt block as the first block, followed by poly[TOCD], with the final block being poly[NORCOOTMS]. The order of polymerization was NORCo block first, followed by the TOCD block, and then the NORCOOTMS block. FTIR of triblock films was performed with a Nicolet 550 FTIR instrument on Teflon sample holders. ^{1}H NMR was performed with a Bruker AM400 spectrometer with d-THF as solvent. Peaks were referenced from THF internal peaks, and no tetramethylsilane (TMS) was

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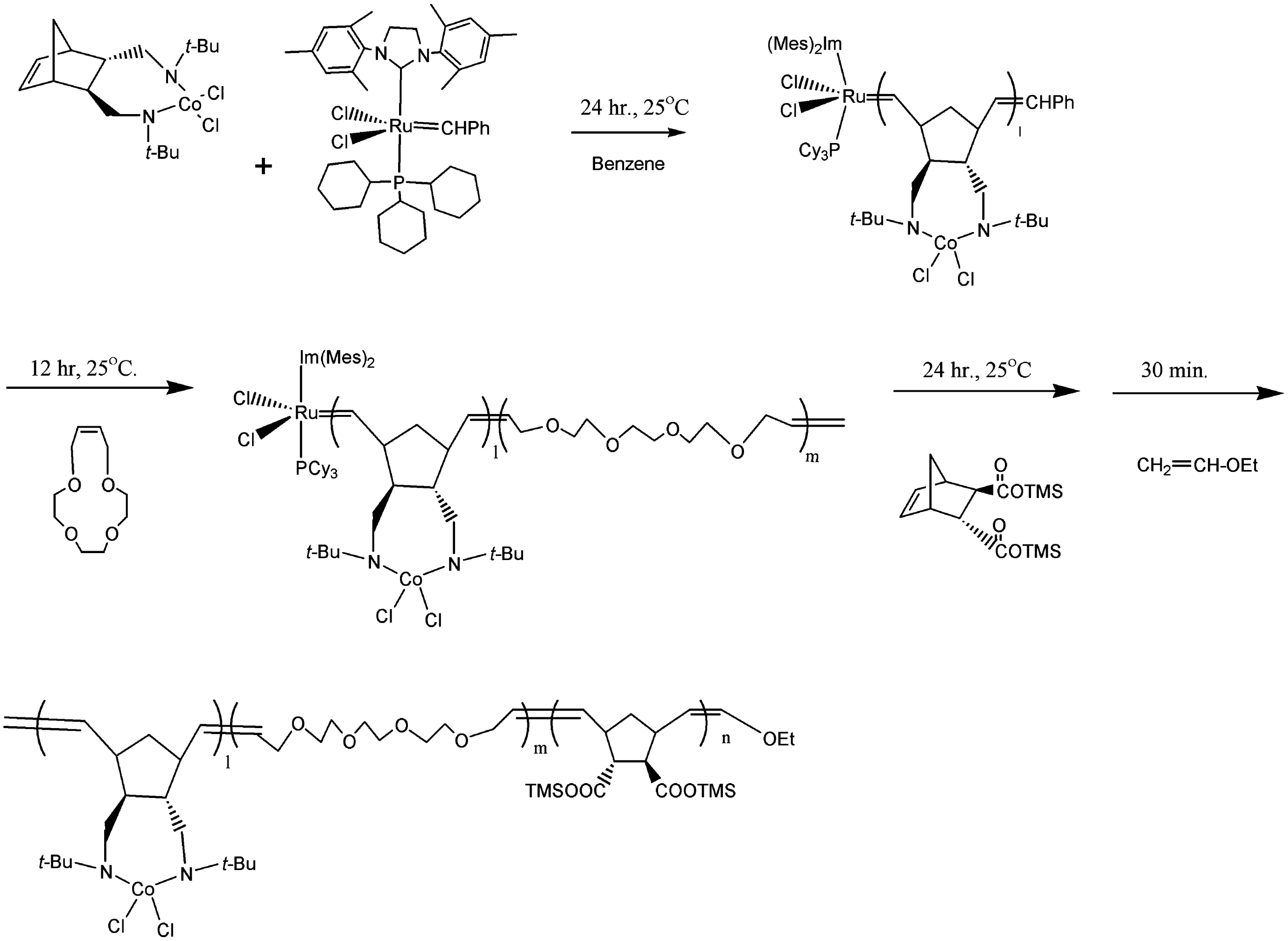

Figure 1. Synthesis schematic of [NORCo]$_{80}$/[TOCD]$_{150}$/[NORCOOTMS]$_{150}$ triblock.

used. UV−vis spectra were obtained with a Varian Cary 5 UV−vis spectrometer. The self-assembly of the cobalt oxide within the triblock copolymer matrix was achieved at room temperature. CoO nanoclusters are formed spontaneously upon reaction of the triblock with water. X-ray photoelectron spectroscopy (XPS) was used to determine the structure of the cobalt oxide. The nanoparticles are formed within the lamellar microphase-separated morphology of the block copolymer, which serves as the templating medium.

Synthesis of Norbornene−Cobalt (Co(bTAN)). Li$_2$(bTAN) (1.0 g, 3.62 mmol) was dissolved in 50 mL of ether. CoCl$_2$ (0.56 g, 4.3 mmol) was dissolved in 56 mL of THF and placed in a 100 mL addition funnel. The Li$_2$(bTAN) solution was placed into a dry ice bath and magnetically stirred. Next, the CoCl$_2$ solution was added dropwise. The reaction mixture was stirred for 1 h at −40 °C. It was then warmed to room temperature and stirred for 2 h, followed by stirring at −40 °C for 24 h. The volatiles were removed under vacuum to leave behind a green blue oil. The oil was transferred back into the glovebox, dissolved in 50 mL of pentane, and filtered to remove lithium chloride and unreacted cobalt chloride. Pentane was then removed under vacuum, and Co(bTAN) was obtained as an green-blue oil. An ^{1}H NMR of the compound is shown in Figure 2. The absence of amine peaks (3.2−3.25 ppm) and broadening of other peaks indicate association of cobalt with the monomer. The results of NMR analysis are summarized in Tables 1 and 2. Elemental analysis indicates carbon, hydrogen, nitrogen, and chlorine all present. Because of the analysis method, exposure to oxygen results, and the cobalt becomes cobalt oxide. When oxygen is analyzed for, it matches the chlorine values, 18.1 Theoretical values were as follows: C, 52.1; Cl, 18.1; H, 7.7; N, 7.1. Values found were the following: C, 29.08; H, 6.5; N, 3.5; Cl, 18.1. A UV−vis spectrum indicates a peak at 605 nm which is due to the cobalt to amine bond.[13] NMR and UV−vis spectra indicate cobalt association with the monomer.

Synthesis of 1,4,7,10-Tetraoxacyclotetradec-12-ene. Diallyl ether triethylene glycol (3.0 g, 13 mmol) was added to 60 mL of anhydrous THF in a 1000 mL oven-dried round-bottom flask. LiClO$_4$ was added and stirred for 30 min. 580 mL of anhydrous, degassed CH$_2$Cl$_2$ was added, followed by 0.537 g of Grubbs's first generation ruthenium catalyst in 10 mL of CH$_2$Cl$_2$. The solution was heated at 40−42 °C for 3 h. The reaction was cooled to room temperature, and 1 mL of ethyl vinyl ether was added. The reaction was stirred for an additional 30 min. The solution was washed with water (2×, 100 mL), dried over MgSO$_4$, and CH$_2$Cl$_2$ removed in vacuo. The crude TOCD product was purified of the residual ruthenium catalyst. Crude TOCD (1.0 g, 4.33 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$. Distilled triethylamine (15 mL, 108 mmol) and tris(hydroxymethyl)phosphine (THP) (5 g, 21.6 mmol) were added to 5 mL of CH$_2$Cl$_2$ and stirred at 40 °C to ensure complete dissolution of the THP. The two solutions were stirred until a color change from brown to yellow was observed. Two water washes (10 mL) were performed, and the aqueous layer became yellow. The layers were separated, and the TOCD was purified by silica gel with ether eluent. A viscous yellow oil was obtained. A table of the NMR peak values is given as Table 3.

Synthesis of 2-Norbornene-5,6-dicarboxylic Acid Bis(trimethylsilyl) Ester (NORCOOTMS). 2-Norbornene-5,6-dicarboxylic acid (NORCOOH) (12 g, 0.066 mol) was dissolved in 550 mL of anhydrous diethyl ether in an argon-purged three-neck flask. 13 mL of dry pyridine (0.164 mol) was added to the solution, and the mixture was stirred for 15 min. 21 mL (0.164 mol) of chlorotrimethylsilane was added over 30 s to the reaction mixture under vigorous stirring. Within 30 min the solution became clear, and pyridine hydrochloride precipi-

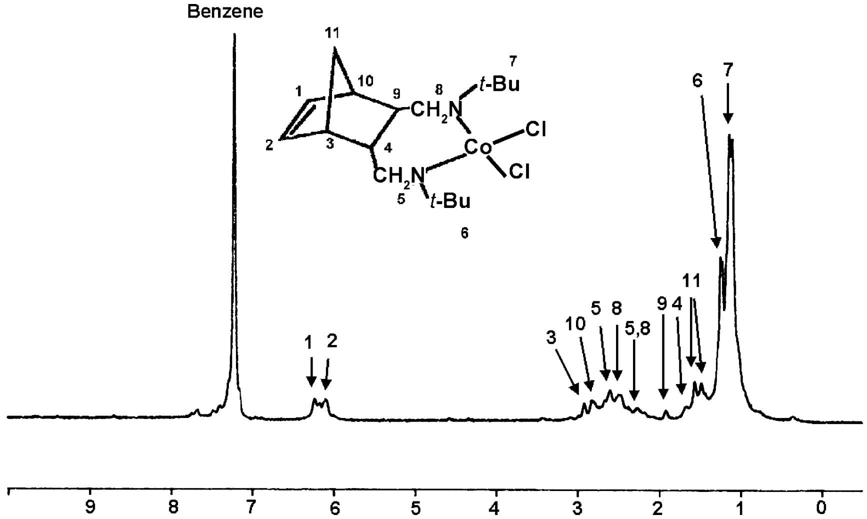

Figure 2. ^{1}H NMR of Co(bTAN) in benzene.

Table 1. Analysis of the ^{1}H NMR of Co(BTAN) in C_6D_6

assigned positions	type of bonds	shifts (ppm)
1	olefinic, =CH	6.16−6.18
2	olefinic, =CH	5.98−6.01
3	bridge head, CH	2.82−2.85
4	exo-methine, CH	1.68−1.68
5	exo-NCH_2	2.20−2.23
		2.48−2.62
6	exo-*t*-Bu	1.13−1.25
7	endo-*t*-Bu	0.98−1.13
8	endo-NCH_2	2.18−2.20
		2.34−2.47
9	endo-methine	1.85−1.91
10	bridge head, CH	2.74−2.79
11	bridge carbon, $C(7)H_2$	1.42−1.55

Table 2. Analysis of the ^{13}C NMR of Co(BTAN) in C_6D_6

assigned positions	type of bonds	shifts (ppm)
1	olefinic, =CH	134.27
2	olefinic, =CH	138.04
3	tertiary C, $NCMe_3$	58.2, 58.5
5	aliphatic C, NCH_2	55.8, 53.5
6	methyl C, C*C* H_3	48.83−45.40
7	methyl C, C*C* H_3	30.0, 29.51

Table 3. Analysis of the NMR of Tetraoxacyclodecene

assigned positions	type of bonds	shifts (ppm)
1	olefinic, =CH	5.86−5.88
2	olefinic, =CH	4.19−4.21
3,4	CH_2	3.62−3.65

Table 4. Analysis of the NMR of NORCOOTMS

assigned positions	type of bonds	shifts (ppm)
1	olefinic, =CH	6.20−6.24
2	olefinic, =CH	5.99−6.03
3, 9	bridge head, CH	2.56−2.58
4	exo-methane, CH	3.08−3.06
5, 6	TMS	0.23−0.28
7	endo-methane	3.29−3.31
8	bridge carbon, CH_2	1.46−1.57

Table 5. Analysis of the ^{13}C NMR of the Triblock Copolymer

assigned positions	type of bonds	shifts (ppm)
1	olefinic, =CH	129.90
2	olefinic, =CH	128.62
3	ether C, CH_2	67.9, 69.0
4	ether C, =CH	72.1, 70.4
5	TMS	2.3−2.8
6	butyl C, C*C* H_3	25.56−25.16
8	bridge carbon, CH_2	1.46−1.57

tated as a white solid. The reaction was allowed to stir for an additional 6 h. The solution was filtered through a bed of Celite (Aldrich) in an argon-filled glovebag. The solvent was removed in vacuo. White NORCOOTMS was transferred into the glovebox and dissolved in anhydrous pentane. Solvent was removed in vacuo. NORCOOTMS was then recrystallized from pentane, followed by recrystallization from ether. At this point, NORCOOTMS was pure enough for polymerization. ^{1}H and ^{13}C NMR values were tabulated.

A/B/C Triblock Copolymer Synthesis. To a stirring solution of 0.25 g of Co(bTAN) in dry, degassed benzene was added 1/150 equiv (2.91 mg) of Grubbs's catalyst (tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidine]ruthenium(IV) dichloride). The solution was allowed to stir for 48 h, and tetraoxacyclotetradecene (0.104 g, 0.514 mmol) was added and allowed to stir for 10 h. The final block of NORCOOTMS was added (0.16 g, 0.514 mmol in 1 mL of benzene) to the polymer reactions. The solution was allowed to stir for 36 h, and the catalyst was cleaved by the addition of 10 μL of ethyl vinyl ether. The solution was allowed to stir for 30 min, and the polymer was precipitated into stirring pentane. ^{1}H and ^{13}C NMR and GPC analyses were performed on the resultant polymer. ^{13}C NMR values are tabulated in Table 5.

Results and Discussion

The ABC triblock copolymer film was cast on Teflon IR cards. In the undoped polymer solution, the carboxylic acid carbonyl peak is located at 1720 cm^{-1}. An amine peak is observed at 3500 cm^{-1}, and the carboxylic acid is observed at 3300 cm^{-1}. Other reference peaks are the C=O stretch at 1720 cm^{-1} and the C−O stretch on the polyether (TOCD) block at 1100 cm^{-1}. The primary peaks corresponding to the amine, NH, the carboxylic acid, hydroxyl, and carbonyl, C=O, and polyether peaks C−O are all observed in the FTIR spectrum. In addition, the vinylic C=C stretch of the polymer backbone is observed at 1600−1640 cm^{-1}. This spectrum corroborates the NMR peaks and helps to further elucidate the chemical structure. ^{1}H NMR in Figure 3 indicates that all the required functional groups are present on the polymer. The protons adjacent to the polyether peaks are clearly shown and occur at 4.0 ppm, marked "C". The unlabeled peaks adjacent to peak "B" are the methine protons and occur in two of the three blocks. In the region of vinylic protons, there are three distinct peaks that correspond to each of the different vinyl protons on the three blocks. TMS peaks are observed

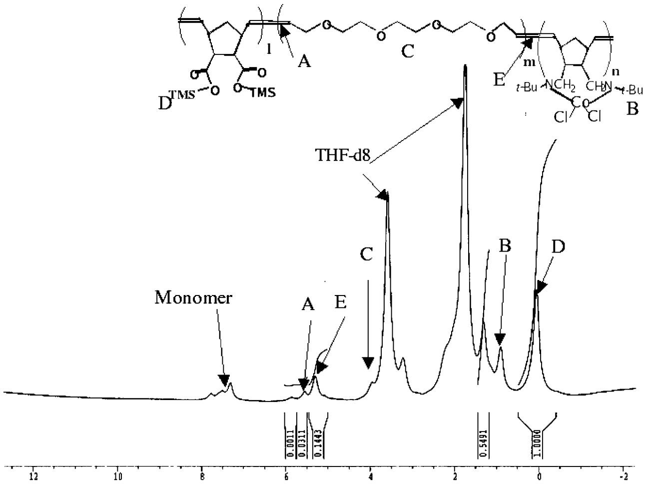

Figure 3. ^{1}H NMR of $[NORCo]_{80}/[TOCD]_{150}/[NORCOOT\text{-}MS]_{150}$.

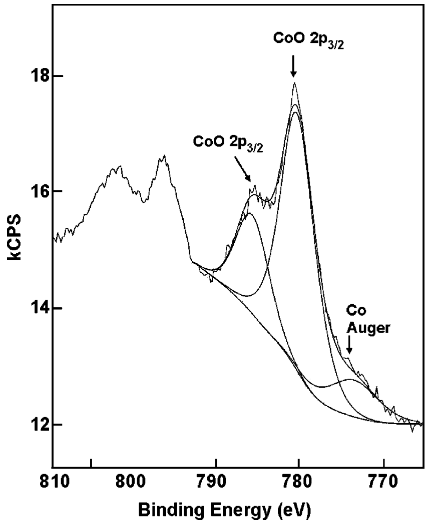

Figure 4. XPS of static cast triblock copolymer films.

at 0.3 ppm and come from the NORCOOTMS block, as the NMR solvent had no TMS internal reference.

XPS was performed to verify the presence of cobalt in the polymer; XPS of the film, treated with water, shows cobalt oxide $2p_{3/2}$ peaks at 781 eV (Figure 4). The cobalt Auger peak is observed at 773 eV, which matches the literature values for cobalt.[15] Cobalt XPS-AES peaks at 1554.0 eV match within 0.5 eV values for CoO.[15]

GPC was performed on the ABC triblock, indicating a unimodal polymer distribution. The polydispersity index of the triblock was 1.93, and the molecular weight was 156 000. The chromatogram is shown as Figure 5. The block ratio determined from GPC of aliquots of the first block synthesized (C), the diblock (BC), and the (ABC) triblock was $[NORCo]_{80}/[TOCD]_{200}/[NORCOOT\text{-}MS]_{180}$. Several catalyst systems are known to polymerize organometallic groups;[3] however, the Grubbs catalyst has not previously been shown to polymerize organometallic monomers. Further study on the organocobalt monomer's effect on the catalyst is underway.

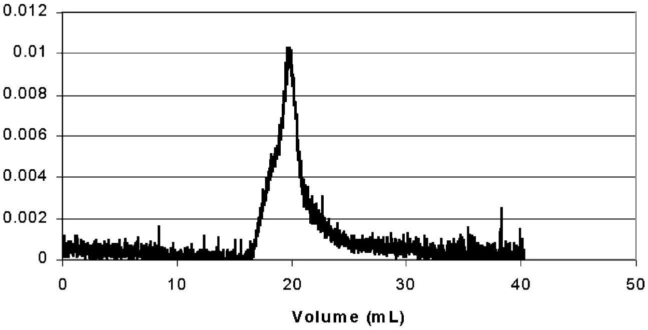

Figure 5. GPC trace of $[NORCo]_{80}/[TOCD]_{150}/[NORCOOT\text{-}MS]_{150}$.

Conclusions

A novel A/B/C triblock copolymer was synthesized, characterized, and treated to obtain a triblock copolymer for potential use as a nanoscale battery. The polymerization was monitored by GPC analysis and NMR. In particular, the ^{1}H NMR shows a shift of the ring-closed vinyl protons to the ring-opened vinyl protons on the polymer backbone. The functionalities observed in a thin film of the polymer were evidenced by FTIR. GPC analysis indicates polymerization has occurred and leads to a unimodal distribution. The formation of cobalt oxide for the anode was verified by XPS.

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