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Catalysts from Self-Assembled Organometallic Block Copolymers**

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Homogenous catalysts are widely used to catalyze chemical reactions in the liquid phase; however, the separation of the reactants and products from such a catalyst can be difficult and often limits their use in practice. For this reason there has been considerable interest in the heterogenization of homogeneous catalysts. The use of polymers for this purpose has been particularly attractive because of the availability of a wide range of polymeric structures and methods for catalyst incorporation.^[1-5] Catalyst heterogenization has been reported by dissolution of the catalyst into the polymer, incorporation of the catalytically active center into the monomer from which the polymer is made, and grafting of the catalyst onto the

chains of a preexisting polymer through chemically active functionalities on the polymer side chain. Here we describe a novel approach for heterogenizing homogeneous catalysts that involves the use of microphase-separated diblock copolymers. Previous studies have demonstrated that nanostructured block copolymers can be used for a wide variety of electronic,^[6] photonic,^[7,8] and electrochemical^[9] applications. Organometallic block copolymers have also been shown to be catalyst precursors for the growth of carbon nanotubes.^[10-12] In the present study, one block is synthesized from a crosslinkable monomer that is not catalytically active, and the second from an organometallic monomer that has the potential to be catalytically active.^[13,14] When placed in a solvent, the polymer gel swells to facilitate transport of the reactants to the active centers and the transport of products from these centers.

The reaction chosen for investigation was the Michael addition of ethyl-2-oxocyclopentane carboxylate (E2OC) and methyl vinyl ketone (MVK) (see Fig. 1). This class of reactions is important for steroid synthesis and for forming C-C bonds in a variety of other organic compounds.^[15] Prior studies have shown that Lewis acids, such as ferric Fe^{III} and scandium Sc^{III} ions, enable the reaction to proceed under mild conditions.^[16-21] In addition, scandium supported on Nafion, polystyrene beads, crosslinked dendrimers, and swollen montmorillonite^[18-21] have also been reported to be effective as catalysts for Michael addition. In this study, we evaluate the activity of the three ferrocenium-based catalysts depicted in Figure 1.

A poly(vinylferrocene-*block*-isoprene) copolymer (FI) was synthesized by sequential anionic polymerization of vinyl ferrocene and isoprene.^[22] This polymer was then oxidized using silver triflate in a benzene/methanol mixture to obtain a poly(vinylferrocenium triflate-*block*-isoprene) (FTI) copolymer, shown in Figure 1d. The oxidation reaction was monitored by UV-vis spectroscopy. Figure 2a shows UV-vis spectra of FTI/benzene mixtures. The absorbance at 638 nm, the wavelength of the ferrocenium cation absorption peak, is a linear function of the molar ratio of added silver triflate to ferrocene moieties (Fig. 2b). This indicates that the fraction of ferrocene oxidized to ferrocenium is directly proportional to the amount of Ag⁺ added. We found that the addition of the silver salt to the FI solution led to an immediate color change from orange to blue. This observation and the data in Figure 2 are consistent with the complete oxidation of the ferrocene (Fc) moieties to ferrocenium (Fc⁺). This is expected because of the large difference in the reduction potentials of Ag⁺ and ferrocenium. After oxidation, the solution was centrifuged, filtered, and freeze-dried. The freeze-dried polymer was then pressed into discs and exposed to electron-beam crosslinking. The dosage on the sample was 58.7 Mrad, which was adequate for crosslinking the polyisoprene block.^[23] All attempts to use other crosslinking strategies, such as peroxide-based crosslinking, were unsuccessful due to the chemical sensitivity of the FT block.

Figure 3 shows a typical transmission electron micrograph of the crosslinked FTI copolymer. The dark phase is the

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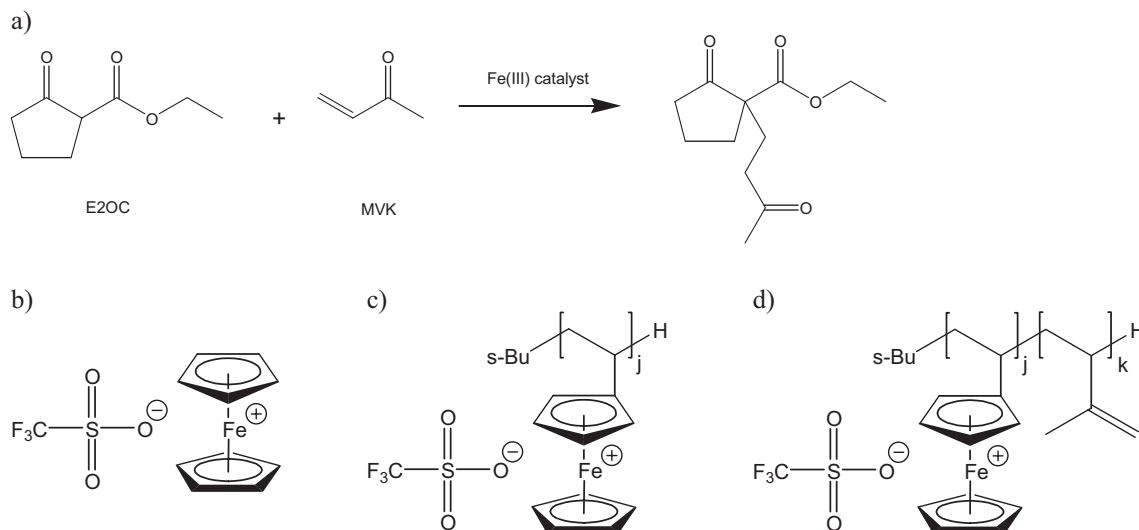


Figure 1. a) Reaction scheme and b–d) molecular structures of the catalysts used in this study. b) Ferrocenium triflate, c) poly(vinylferrocenium triflate), and d) poly(vinylferrocenium triflate-*block*-isoprene).

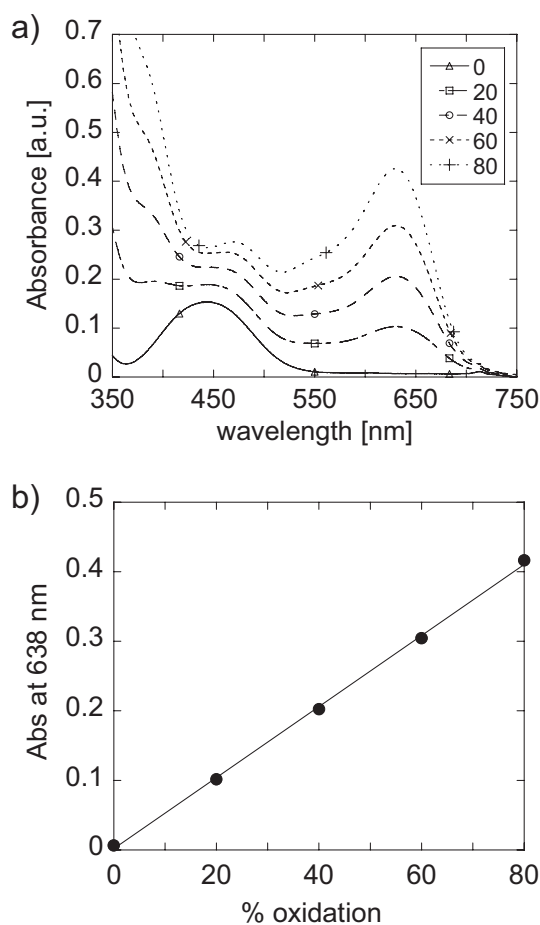


Figure 2. a) UV-vis spectra of 0.1 wt.-% FTI copolymer solutions in benzene for different oxidation percentages. b) The absorbance at 638 nm, the wavelength of the ferrocenium cation absorption peak, versus percent oxidation.

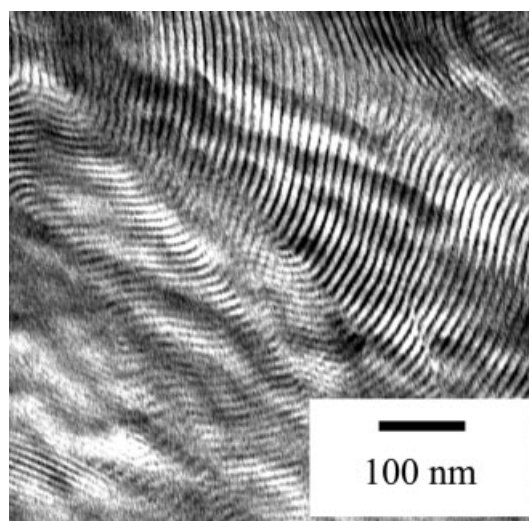


Figure 3. Transmission electron micrograph of the crosslinked poly(vinylferrocenium triflate-*block*-isoprene) copolymer showing a periodic lamellar phase. The catalytically active poly(vinylferrocenium triflate) block appears dark and the supporting polyisoprene block appears light.

poly(vinylferrocenium triflate) block while the light phase is the polyisoprene block. The presence of a periodic lamellar phase with a periodicity of 11 nm is evident in the micrograph. The volume fraction of the FT block in the FTI copolymer, f , is estimated by ¹H NMR to be 0.3.^[24] Uncharged, organic block copolymers with $f=0.3$ form cylindrical phases.^[25] The formation of a lamellar phase in the FTI melt is perhaps due to the presence of counter ions and the stiffness of the FT block.

A predetermined amount of the crosslinked FTI copolymer was placed in an excess of the reaction solvent (6:1 by volume mixture of dichloromethane/methanol) to swell for 24 h. The

volume of the swollen gel was a factor of 14 larger than that of the dry gel, indicating that the solvent mixture is a good solvent for the gel. All of the chains that are not attached to the crosslinked network are removed in this step. The gel fraction, f_{gel} , defined as the ratio of the weight of the dry sample after the swelling experiment to that before the swelling experiment, was 0.52. This measured gel fraction is indicative of a lightly crosslinked network which is expected to promote mass transfer. After the extraction of the chains not attached to the network, no evidence of metal leaching was observed.

The catalytic activity of crosslinked FTI was compared with that of ferrocenium triflate, poly(vinylferrocenium triflate), and the uncrosslinked FTI copolymer. The concentration of active sites Fe^{III} (M_{Fc^+}) in the reaction mixtures was 8.1 mM in the case of the homogeneous catalysts, and ($f_{\text{gel}} \times M_{\text{Fc}^+}$) 4.2 mM in the case of the crosslinked FTI catalyst. Experiments with different concentrations of E2OC and MVK demonstrated that the reaction is pseudo-first order in MVK. These kinetics suggest that E2OC reacts reversibly with the catalyst to form an adduct, which then reacts more slowly with MVK. The time-dependence of the MVK concentration in the presence of crosslinked FTI is shown in Figure 4. The cluster of points at a given time represents data obtained from independent reagent/catalyst mixtures. The decay of MVK

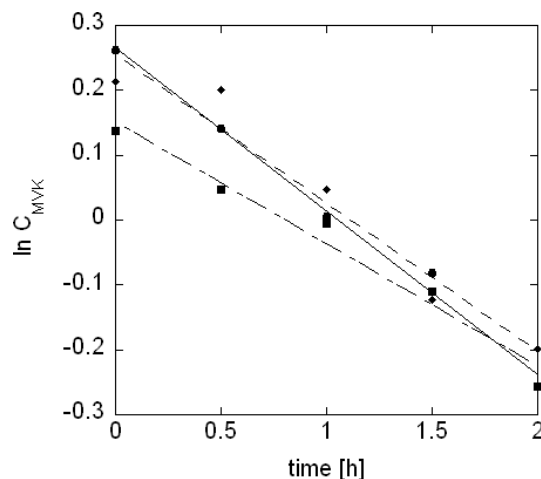


Figure 4. Reactant (MVK) concentration (molar) versus time on a semi-log plot for three independent Michael addition reactions catalyzed by crosslinked FTI. The slope of least squares linear fits through the data determine the apparent first-order reaction rate constant.

concentration is approximately exponential, as shown in Figure 4, and this enables determination of the apparent first-order reaction rate constant k . Qualitatively similar data were obtained for the other catalysts shown in Figure 1. The rate constants thus obtained from the four catalyst systems of interest are listed in Table 1. Our values of k , after normalization for the concentration of active sites, range from 52–64 $\text{h}^{-1} M_{\text{Fc}^+}^{-1}$. These values are similar in magnitude to the rates reported for the iron(III) chloride catalyst.^[17] We have

Table 1. Michael reaction rate constants obtained for four catalyst systems described in the text.

Catalyst	k [$\text{h}^{-1} M_{\text{Fc}^+}^{-1}$]
Ferrocenium triflate	55 ± 7
Poly(vinylferrocenium triflate)	64 ± 2
FTI	52 ± 5
crosslinked FTI gel	53 ± 4

thus clearly established the catalytic activity of our self-assembled heterogeneous catalyst. The similarity of k values obtained from heterogeneous and homogeneous catalysts indicates that the activity of our heterogeneous catalyst is not mass-transfer limited.

To summarize, we have established a new route for synthesizing catalysts using organometallic block copolymers. The catalysts are formed by molecular self-assembly, which enables stringent control over the size and arrangement of both the active sites and the support structure. The polymer block that is free of active centers is crosslinked in order to provide support for the polymer block containing the catalytically active centers. This is functionally similar to the synthesis of mesoporous siliceous materials created by an amphiphilic, structure-directing agent,^[26,27] in which the latter is retained rather than being sacrificed and is catalytically active. However, in contrast to the use of an inorganic support, the rigidity of the support can be altered by changing the crosslinking dosage, providing greater capacity for tuning the access to the catalytically active centers. Further investigation of the catalyst structure in solution and the effect of support and active-site geometry on catalytic activity and selectivity will be undertaken.

Experimental

Polymer Synthesis: A poly(vinylferrocene-*block*-isoprene) copolymer (FI) was synthesized by sequential anionic polymerization under high vacuum in THF, using *sec*-butyl lithium as the initiator. 1.9 g of vinyl ferrocene purified via double sublimation was added to solvent and 0.45 mL 1.4 M *sec*-butyl lithium solution. The polymerization was allowed to proceed at -40°C for 24 h to ensure complete conversion of vinyl ferrocene. Next, 4.2 g of isoprene purified over calcium hydride and *sec*-butyl lithium was vacuum-distilled into the reaction mixture. The added isoprene was allowed to react for 8 h at 0°C in order to assure its complete consumption. The polymerization was then terminated with isopropyl alcohol in an argon glove box. 2 g of polyvinylferrocene homopolymer was also synthesized by the above method. Gel permeation chromatography (GPC) measurements of the FI copolymer show a weight-average molecular weight (M_w) of $12\,000 \text{ g mol}^{-1}$ and a polydispersity index (PDI) of 1.11. GPC was also performed on the polyvinylferrocene homopolymer with $M_w = 3300 \text{ g mol}^{-1}$ and PDI = 1.02. $^1\text{H NMR}$ was performed on the FI copolymer. Peak integrations show 77% 1,4-addition of isoprene and a ratio of isoprene-to-vinylferrocene repeat units of 8.3:1.

Oxidation: 0.9 equivalents of silver triflate (AgSO_3CF_3) dissolved in methanol was mixed inside an argon glove box with a benzene/FI solution to obtain a poly(vinylferrocenium triflate-*block*-isoprene) copolymer (FTI). All solvents were thoroughly degassed prior to use.

After oxidation, the solution was centrifuged, decanted, and filtered through a 0.2 μm filter to remove silver particles, and freeze-dried for storage. Polyvinylferrocene homopolymer and ferrocene were oxidized in the same manner.

Crosslinking: The freeze-dried FTI copolymer was molded mechanically into disks with diameter = 7 mm and thickness = 1 mm. Electron-beam crosslinking of the polymer was performed using an electron-beam source at Tyco Electronics in Menlo Park, CA. The samples were irradiated by a 3 MeV beam source using a series of approximately 0.9 s exposures for a total exposure time of 19.8 s.

Transmission Electron Microscopy: Thin sections (ca. 50 nm) of crosslinked FTI were cryomicrotomed at -100°C and examined by transmission electron microscopy at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory (LBNL). Staining was not required, since the electron contrast between the iron-containing block and the organic block was sufficient to differentiate the microphases of the polymer.

Activity Measurements: Equimolar mixtures of reactants (0.29 mL MVK and 0.50 mL E2OC) were added to 2 mL of solvent (6:1 by volume dichloromethane:methanol mixture). Predetermined amounts of catalysts were added at time zero ($t=0$) to the reaction mixture. The swollen crosslinked FTI catalyst was added as cubes approximately 1 mm in length. The Michael addition reaction was carried out in a glass reaction vessel at room temperature in an argon atmosphere. Samples were pipetted out of the glass reactor at regular intervals and analyzed by ^1H NMR. The progress of the reaction was followed by the time dependence of the vinyl proton NMR signal at 6.3 ppm, which is proportional to the concentration of the MVK. The samples obtained from the homogeneous catalysts were filtered through alumina columns to remove the dissolved iron species that interfere with the NMR experiments. In the case of the crosslinked FTI catalyst, no iron removal was needed prior to the NMR analysis. Since 10% of the ferrocene in FTI remained after oxidation of the ferrocene to ferrocenium, and a small amount of silver may have been trapped in the block copolymer after filtration, experiments were carried out to determine whether ferrocene or silver are catalytically active. Neither of these components was found to be active for Michael addition under the conditions used for this work.

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Stainless-Steel-Net-Supported Zeolite NaA Membrane with High Permeance and High Permselectivity for Oxygen over Nitrogen**

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Zeolites with uniform micropores have been used as selective catalysts and adsorbents owing to their ability to permit small molecules to enter their pores while leaving larger molecules behind, or to allow small molecules to pass through the pores prior to larger molecules.^[1] In the past ten years, much effort has been made to develop zeolite membranes for separation and catalysis applications.^[2–11] Zeolite NaA possesses

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