2-2002

Oxidative polymerization of 1,4-diethynylbenzene into highly conjugated poly(phenylene butadiynylene) within the channels of surface-functionalized mesoporous silica and alumina materials

Victor S.-Y. Lin
Iowa State University

Daniela Rodica Radu
Iowa State University

Mi-Kyung Han
Iowa State University

See next page for additional authors

Follow this and additional works at: http://lib.dr.iastate.edu/cbe_pubs

Part of the Chemical Engineering Commons, and the Chemistry Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/cbe_pubs/223. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Oxidative polymerization of 1,4-diethynylbenzene into highly conjugated poly(phenylene butadiynylene) within the channels of surface-functionalized mesoporous silica and alumina materials

Abstract
A polyalkynylene-based conducting polymer (molecular wire) has been synthesized within the Cu-functionalized mesoporous MCM-41 silica catalyst. Fluorescence and 13C solid-state NMR provided spectroscopic evidence that the synthesis of extended polymeric chains with a high degree of alignment requires homogeneously distributed catalytic sites throughout the entire MCM matrix. This type of homogeneity has been achieved via co-condensation of the catalytic groups in narrow pores. In addition, our results indicated that proper adjustment of the pore diameter is vital to prevent clogging of the pores with aggregated or cross-linked polymers or both.

Keywords
aluminum oxide, benzene derivative, copper complex, poly(phenylene butadiynylene), silicon dioxide, carbon nuclear magnetic resonance, desorption, Ames Laboratory, Department of Chemistry

Disciplines
Chemical Engineering | Chemistry

Comments
This is an article from Journal of the American Chemical Society 124 (2002): 9040, doi: 10.1021/ja025925o. Posted with permission

Authors
Victor S.-Y. Lin, Daniela Rodica Radu, Mi-Kyung Han, Weihua Deng, Shigeki Kuroki, Brent H. Shanks, and Marek Pruski
Oxidative Polymerization of 1,4-Diethynylbenzene into Highly Conjugated Poly(phenylene butadiynylene) within the Channels of Surface-Functionalized Mesoporous Silica and Alumina Materials

Victor S.-Y. Lin, Daniela R. Radu, Mi-Kyung Han, Weihua Deng, Shigeki Kuroki,
Brent H. Shanks, and Marek Pruski

Department of Chemistry, Department of Chemical Engineering, and Ames Laboratory, Iowa State University, Ames, Iowa 50011

Received February 13, 2002

Properly functionalized and structurally ordered mesoporous materials, such as MCM-type silicas and aluminas, with tunable pore size and narrow pore-size distributions have attracted much attention for their potential applications as new catalytic scaffolds to direct and orient the conformation of desired products. For example, recent interest in encapsulation or synthesis or both of conducting polymers within the channels of MCM-41 has highlighted the future application of these materials as directional electron/energy transfer nanodevices. However, several fundamental obstacles, such as low content and lack of the structural alignment of these polymer materials within the porous hosts, have yet to be overcome. Herein, we report the synthesis of Cu\textsuperscript{2+}-functionalized MCM-41 silica and alumina, with different pore diameters, which can oxidatively catalyze the formation of a highly conjugated poly(phenylene butadiynylene) polymer (PPB)\textsuperscript{2} as depicted in Figure 1. The alignment and extent of the conjugation of the conducting polymer within the mesoporous materials were characterized.

Previous studies on the electronic properties of polyalkynylene-based conducting polymers, such as poly(phenylene ethynylene) (PPE) and PPB, demonstrated that these supermolecules have very high conductivity and charge/weight storage capability, when suitably doped.\textsuperscript{3} Utilizing the mesoporous channels as catalytic nano-reactors for the fabrication of highly conjugated polyalkynlenes will stabilize their architecture in the desired, aligned form.

Clearly, the rate and extent of polymerization within the mesoporous channels of MCM-41 directly depend on (1) the amount and spatial distribution of catalytic sites and (2) the diffusion rate of monomeric precursors and their local concentration near the catalytic sites. Both factors can be adjusted by varying the pore size and by tailoring the catalytic activity of the surface through proper functionalization. To examine how these factors influence the oxidative polymerization of 1,4-diethynylbenzene, we synthesized two mesoporous silica and alumina materials (Cu-MCM and Cu-MAL, respectively) with different pore sizes and tested two different methods of Cu\textsuperscript{2+} surface functionalization.

Several approaches to surface functionalization of mesoporous materials have been reported, including direct grafting, impregnation, and co-condensation. Direct grafting and impregnation to the as-synthesized MCM-41 silicas usually give rise to an inhomogeneous surface coverage of the functional groups.\textsuperscript{4} Most of the incorporated functional groups are located on the exterior surface or at the opening portion of the porous channels. In contrast, the co-condensation method yields a more homogeneous distribution of the functional groups within the mesopores.\textsuperscript{5}

Thus, we prepared the Cu\textsuperscript{2+}-incorporated MCM-41 silica material (Cu-MCM) by co-condensation using a Cu\textsuperscript{2+}-chelating molecule, N-[3-(trimethoxysilyl)propyl]ethylenediamine, as the precursor.\textsuperscript{2} The powder XRD, \textsuperscript{6} BET N\textsubscript{2} sorption isotherm, and BJH pore-size distribution measurements indicated that the Cu-MCM contains a typical MCM-41-type of ordered cylindrical porous structure with a high surface area of ca. 655.0 m\textsuperscript{2}/g and a BJH average pore diameter of ca. 25.6 Å (Figure 2a,b). A mesoporous alumina catalyst was also synthesized using a method reported earlier\textsuperscript{2} followed by Cu impregnation (Cu-MAL). The mesoporous structure of Cu\textsuperscript{2+}-alumina catalyst was also characterized with aforementioned spectroscopic methods and exhibits a surface of ca. 448.0 m\textsuperscript{2}/g and a BJH average pore diameter of ca. 68.0 Å (Figure 2c,d). The amounts of Cu\textsuperscript{2+} catalytic sites of both Cu-MCM and Cu-MAL were quantified to be ca. 5.2 × 10\textsuperscript{-4} and 1.3 × 10\textsuperscript{-5} mol/g, respectively.\textsuperscript{6}

Our studies of 1,4-diethynylbenzene polymerization with the two Cu\textsuperscript{2+}-functionalized mesoporous catalysts gave very different results. In the case of Cu-MCM, a 245-nm bathochromic shift (emission \(\lambda_{\text{max}} = 643.5\) nm) of the fluorescence emission spectra of the PPB polymer was observed after 56 h of refluxing in pyridine (Figure 3). The result indicates the effective \(\pi\)-conjugation length of the PPB polymer synthesized within the mesoporous channels of Cu-MCM is perhaps comparable to that of PPBs synthesized in homogeneous solutions.\textsuperscript{8} Interestingly, the oxidative polymerization using Cu-MAL showed two bathochromic-shifted fluorescence peaks (\(\lambda_{\text{max}} = 472.5\) and 551.5 nm) under the same reaction conditions. However, both shifts are significantly smaller than in the case of Cu-MCM. This spectral difference is consistent with

---

\textsuperscript{9} To whom the correspondence should be addressed. E-mail: vsylin@iastate.edu.
\textsuperscript{1} Department of Chemistry.
\textsuperscript{2} Department of Chemical Engineering.
\textsuperscript{3} U.S. DOE Ames Laboratory.
The arrangement of the synthesized structures has been obtained using polymerization indeed occurred, direct evidence of the spatial distribution of the PPB polymers synthesized by both catalysts also confirmed. Other photophysical and MALDI mass spectroscopy measurements were carried out using $^{13}$C solid-state NMR. The measurements were carried out using $^{13}$C spectra of the studied distributions of the Cu-MAL probe. Three representative $^{13}$C spectra of the studied samples are shown in Figure 4. The spectrum of a sample catalyzed with Cu-MAL (a) is notably different from those of a randomly oriented polymer (c) and a polymer that was synthesized with the Cu-MAL material (b). The former is well resolved and consists of four resonance lines, which are assigned as shown in the figure. The spectrum of bulk polymer exhibits considerable line broadening, with only two resolved bands at around 80 and 130 ppm, corresponding to sp and sp$^2$ carbons, respectively. The observed broadening reflects the conformational heterogeneity in the three-dimensional arrangements of polymeric chains. The same morphology is observed in the case of Cu-MAL. Additional significant differences are observed in spectra (b) and (c) with respect to (a): (i) both resonances are not only broader, but comprise more than two lines, and (ii) the intensities of sp$^2$ and sp bands do not match the 3:2 ratio expected for PPB. These spectral features are consistent with considerable polydiacetylene-type cross-linking that occurred in the bulk polymer and Cu-MAL. In the case of Cu-MCM, the sharpness of the observed resonances and lack of cross-linking demonstrate that isolated molecular wires are formed within the parallel channels of MCM-41.

We have demonstrated that a linearly aligned conducting polymer can be catalytically synthesized within the porous channels of MCM-41 silica. Fluorescence and solid-state NMR provided spectroscopic evidence that the synthesis of extended polymeric chains with a high degree of alignment requires homogeneously distributed catalytic sites throughout the entire matrix. This type of homogeneity has been achieved via co-condensation of the catalytic groups in narrow pores.

Acknowledgment. We thank the Biotechnology Office of ISU for startup funds and U.S. DOE, Office of BES, for support of this work through contract W-7405-Eng-82.

Supporting Information Available: Experimental details, XRD measurements, UV/vis absorption spectra, and MALDI mass spectroscopy measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

Figure 2. Nitrogen adsorption/desorption isotherms and the pore size distributions of the Cu–MCM, (a), (b), and Cu–MAL, (c), (d), materials before (solid line) and after (dashed line) PPB polymerization within the mesoporous channels.

Figure 3. Normalized fluorescence emission spectra of 1,4-diethynylbenzene (dotted line) and the PPB-containing composite materials of Cu-MAL and Cu–MCM catalysts (dashed and solid lines, respectively) after 56 h of polymerization.

Figure 4. $^{13}$C CPMAS spectra of (a) a structurally aligned PPB polymer catalyzed by Cu–MCM, (b) a PPB polymer synthesized with Cu-MAL, and (c) bulk PPB. The spectra were measured at room temperature, using 4080 scans, 10-s intervals, sample rotation rate of 5 kHz, contact time of 2 ms, CW $^1$H decoupling at 70 kHz and sideband suppression (TOSS).

smaller $\pi$-conjugation of the PPB polymer in the case of Cu-MAL. Other photophysical and MALDI mass spectroscopy measurements of the PPB polymers synthesized by both catalysts also confirmed the significant difference in the degree of polymerization.

While the aforementioned results clearly established that the polymerization indeed occurred, direct evidence of the spatial arrangement of the synthesized structures has been obtained using $^{13}$C solid-state NMR. The measurements were carried out using $^1$H–$^{13}$C cross polarization (CP) at 100.6 MHz on a Chemagnetics Infinity spectrometer equipped with a 5-mm magic angle spinning (MAS) probe. Three representative $^{13}$C spectra of the studied samples are shown in Figure 4. The spectrum of a sample catalyzed by Cu–MCM (a) is notably different from those of a randomly oriented polymer (c) and a polymer that was synthesized with the Cu-MAL material (b). The former is well resolved and consists of four resonance lines, which are assigned as shown in the figure. The spectrum of bulk polymer exhibits considerable line broadening, with only two resolved bands at around 80 and 130 ppm, corresponding to sp and sp$^2$ carbons, respectively. The observed broadening reflects the conformational heterogeneity in the three-dimensional arrangements of polymeric chains. The same morphology is observed in the case of Cu-MAL. Additional significant differences are observed in spectra (b) and (c) with respect to (a): (i) both resonances are not only broader, but comprise more than two lines, and (ii) the intensities of sp$^2$ and sp bands do not match the 3:2 ratio expected for PPB. These spectral features are consistent with considerable polydiacetylene-type cross-linking that occurred in the bulk polymer and Cu-MAL. In the case of Cu–MCM, the sharpness of the observed resonances and lack of cross-linking illustrate that isolated molecular wires are formed within the parallel channels of MCM-41.

We have demonstrated that a linearly aligned conducting polymer can be catalytically synthesized within the porous channels of MCM-41 silica. Fluorescence and solid-state NMR provided spectroscopic evidence that the synthesis of extended polymeric chains with a high degree of alignment requires homogeneously distributed catalytic sites throughout the entire matrix. This type of homogeneity has been achieved via co-condensation of the catalytic groups in narrow pores.

Acknowledgment. We thank the Biotechnology Office of ISU for startup funds and U.S. DOE, Office of BES, for support of this work through contract W-7405-Eng-82.

Supporting Information Available: Experimental details, XRD measurements, UV/vis absorption spectra, and MALDI mass spectroscopy measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References


8. See Supporting Information for UV/vis absorption spectra and MALDI mass spectroscopy measurements of the PPB polymers synthesized by the Cu–MCM and Cu-MAL.


JA025925O