A direct synthesis of the styrylimido derivative of the hexamolybdate dianion

Jeffrey Fischer, Tiffany Stampka and Mark F. Roll

Department of Chemical & Materials Engineering, The University of Idaho, Moscow, ID 83844, USA

Polyoxometalate imides represent an area of materials chemistry research that recently has seen exciting exploration. Consisting of polyhedral metal-oxide clusters covalently coupled to organic ligands, they possess a combination of electrochemical activity and poly-anionic character hint. These characteristics suggest significant opportunities in the area of solid-electrolytes, particularly if the typically good film forming characteristics of hybrid polymers can be accessed. The incorporation of a styryl group allows for hybrid polymers to be synthesized through free radical methods, producing hybrid materials that offer an enormous number of opportunities to both materials scientists and engineers. This Note will document a concise route to quickly produce the readily polymerizable, styrylimido-hexamolybdate monomer from low cost precursor materials by leveraging recent advances and address some of the synthetic challenges found.

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1. Introduction

Hybrid materials offer an enormous number of opportunities to both materials scientists and engineers.1–4 Polyoxometalates represent a unique set of metal-oxide clusters5–7 that can be covalently coupled with organic ligands, an area of research that has seen extensive, exciting exploration.8–17 The review of polyoxometalate chemistry given by Katsoulis outlines specific applications of these inorganic clusters, including a variety of high-value applications from electrodes to gas sensors to fuel cells.5 The combination of electrochemical activity and dianionic character hint at significant opportunities in the area of electrochemical cells, particularly if the better film forming characteristics of hybrid polymers can be accessed.17

The addition of a polymerizable styryl ligand to a hexamolybdate cluster (Fig. 1) and the demonstration of its free radical polymerization by the Maatta group cracked open the door to an enormous variety of polymeric hybrid polyoxometalate imides.17 This Note will document a concise route to rapidly synthesize a readily polymerizable, styryl-polyoxometalate monomer from low cost precursor materials using recent discoveries in the area of polyoxometalate imidization.

As mentioned, the monomer of interest (1) has been reported previously, however the reported synthesis is relatively complex, requiring synthesis of an iminophosphorane intermediate and a 5 day reaction period.17 The synthesis reported herein utilizes recent synthetic developments with a precipitation based work-up to provide facile access to monomer 1 in a matter of a few hours, opening opportunities for a wider set of polymer and materials chemistry researchers (Scheme 1).

The inorganic core, is the hexa-molybdate Lindqvist dianion, whose general synthesis was well-documented by Klemperer.18 We extend the reach of this synthesis by documenting a sonochemical19 route, wherein the polyoxometalate cluster synthesis is completed in minutes (10×–50× faster). Key benefits of ultrasound driven reactions are shorter reaction times, particularly at the multi-gram scale. Similar accelerations are not uncommon in sonochemical explorations,19 and future examples of in the area of hybrid materials can also be expected.

The covalent grafting of the organic styryl group presented here is an extension of the flexible dicyclohexylcarbodiimide-driven imidization documented and extended by the Wei and co-workers.14–16 Previous examples have focused on imidization by 2,6- or 2,4- functionalized anilines, with reaction times (at reflux) in the range of 12–24 h. Previous imidizations have relied on isocyanate or iminophosphorane precursors with multi-day reaction times,17 so these reports represent a significant step forward in providing access to polyoxometalate hybrids.

2. Experimental

2.1 Materials and general methods

All chemicals purchased were of analytical grade, and were used without further purification. Sonication was performed with
a Sonics and Materials VC750 Ultrasonic Processor. FTIR was performed using Thermo Scientific Nicolet 6700 FTIR with 32 scans, a data spacing of 1.928 cm⁻¹, and blank KBr cards used for a baseline. ¹H NMR spectra were obtained using a Bruker Avance 300 mHz NMR Spectrometer at 8 scans with 32768 points and resolved with the Spinworks 3.8.1 program. Elemental analysis was done with an Exeter Analytical Inc. CE-440 Elemental Analyzer. Mass spectra were obtained from samples analyzed directly by electrospray ionization-mass spectrometry (ESI-MS) following dissolution in acetonitrile. The sample was introduced to a Finnigan LCQ-Deca instrument (Thermoquest) at a flow rate of 10 μL min⁻¹. Both negative and positive ion ESI-MS scans in the range m/z 150–2000 were performed for the same sample. The ion source and capillary voltages were 4.48 kV and 47 V, respectively, and the temperature was 275°C.

2.1.1 Tetrabutylammonium hexamolybdate, (n-Bu₄N)₂Mo₆O₁₉, via Sonication

A solution of 2.51 g (10.4 mmol) sodium molybdate dihydrate (Na₂MoO₄·2H₂O) in 10 mL of water is acidified with 3 mL of 6 N aqueous HCl (18 mmol) in a 50 mL Erlenmeyer flask while stirring over a 1-min period at room temperature. A solution of 1.21 g (3.75 mmol) of tetrabutylammonium bromide in 2 mL of water is then slowly added over a 1-min period while stirring to form an immediate formation of a white precipitate. This solution is allowed to stir for 5 min and is then placed under continuous sonication at 40% amplitude (~30 watts) for 15 min, reaching a solution temperature of 65°C.

During this period the white solid changes to yellow. The yellow solution mixture is collected with solution temperature of 65°C. During this period the white solid is allowed to stir for 5 min and is then placed under continuous sonication at 40% amplitude (~30 watts) for 15 min, reaching a solution temperature of 65°C.

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The resulting filtrate and the crude product was obtained upon filtration and washed with three 20 mL portions of water.

While these data were consistent with the published results, the X-ray powder pattern calculated from the published single crystal structure. (See S.I.) This short reaction time in comparison to previously reported imidization reactions using 2,4- and 2,6-dimethylaniline is likely a result of lower steric hindrance and electronic activation, however definitive explorations to ascertain the critical details are yet to be documented.

While these data were consistent with the published results, with Reviewer prompting, mass spectrographic data not reported in the original reference were obtained. Qualitative analysis of 100°C for 3h after adding the 4-vinylaniline and DCC, after which it was cooled to room temperature. A white precipitate of 1,3-dicyclohexylurea was removed by vacuum filtration. The resulting filtrate was dripped into 50 mL stirring ethanol over a 1-min period, slowly forming an orange precipitate. 5 mL water was dripped into the stirring ethanol solution over a 1-min period to further precipitate the orange material. The orange precipitate was vacuum filtered and the crude product was obtained upon evaporation overnight to give an orange powder (yield: ca. 54% based on Mo).

³H NMR [(CD₃)₂SO]: δ 7.57, 7.54, 7.20, 7.18 (AA'BB' 'quartet', 4H, CH₄), 6.78 (m, 1H, CH), 5.85 (d, 1H =CH₂), 5.28 (d, 1H =CH₂), 3.17 (m, NCH₂, 16H), 1.58 (m, CH₂, 16H), 1.37 (m, CH₂, 16H), 0.95 (t, CH₃, 24H). Anal. Calcd. for C₃₂H₇₂N₄Mo₆O₁₉: C, 28.17; H, 5.32; N, 2.05. Found: C, 32.81; H, 5.42; N, 3.09.

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3. Results and discussion

While not previously reported to our knowledge, we find the use of 2,2-dimethoxypropane (DMP) to dehydrate the acetonitrile solution of the di-tetrabutylammonium salt of the hexamolybdate (TBAmo) in situ prior to the addition of the 4-aminoanisole (AS) and dicyclohexylcarbodiimide (DCC) significantly facilitates successful imidization. Following this dehydration pretreatment, the imidization of AS with TBAmo can be accomplished in less than three hours using traditional heating methods.

Table 1 shows the experimental matrix explored, wherein the degree of substitution is computed from the ¹H-NMR integrations of the aromatic imide and tetrabutylammonium protons.

All ¹H-NMR, elemental analysis and FT-IR data are consistent with the previous report. Powder X-ray diffraction data indicate isolation of a potential polymorph, when compared to the X-ray powder pattern calculated from the published single crystal structure. (See S.I.) This short reaction time in comparison to previously reported imidization reactions using 2,4- and 2,6-dimethylaniline is likely a result of lower steric hindrance and electronic activation, however definitive explorations to ascertain the critical details are yet to be documented.

While these data were consistent with the published results, with Reviewer prompting, mass spectrographic data not reported in the original reference were obtained. Qualitative analysis
indicates that up to 30% of the crude product consists of unsubstituted and di-substituted polyoxometalate clusters (See, S.I.). Recrystallization from acetone has been found to reduce the content of unsubstituted polyoxometalates, but further purification studies will be required to isolate a pure molecular species. Regardless, it seems clear that substantial discoveries remain in the area of polyoxometalate imidization, with critical import for their application as Hybrid Materials.

With a concise styryl-imidization of the hexamolybdate dianion, a broad set of investigations can be readily be envisioned from the possibilities presented by the incorporation of I into cross-linked ion exchange resins to block copolymers produced through controlled radical polymerization. The latter hold significant potential in the formation of nano- and meso-structured polymer thin-films and monoliths.\(^{21}\) Already, similar vinyl functionalized polyoxometalates have been investigated as lithographic materials\(^{22,23}\) but are practically unexplored potential in this area to enable nanometer scale patterning through electron beam or extreme ultraviolet lithography provide significant impetus to further exploration.

4. Conclusion

This note presents a concise route the styryl-imide of the hexamolybdate dianion, with applications from ion-exchange resins to block co-polymers to lithographic resists. The key to this route is the combination of sonochemical preparation, in-situ dehydration and dicyclohexylcarbodiimide-driven imidization. This should significantly lower the barrier for further investigations by a broad array of polymer and materials scientists, and encourage exploration of the untapped potential of these hybrid materials.

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Table 1. Experimental matrix for imidization studies

| Run   | TBAMo (mmol) | Equiv 4, AS | Equiv DCC | DMP (mL) | CH₃CN (mL) | Run Time (hrs) | Degree of Substitution | Yield (based on Mo) |
|-------|--------------|-------------|------------|----------|------------|---------------|-----------------------|-------------------|
| MSI 5 | 0.37         | 2.28        | 1.45       | 0.5      | 7          | 20            | 1.0                   | 51%               |
| MSI 8 | 0.37         | 2.27        | 1.49       | 0.5      | 7          | 4             | 1.0                   | 42%               |
| MSI 9 | 0.37         | 2.18        | 1.43       | 0.5      | 7          | 4             | 1.0                   | 50%               |
| MSI 10| 0.37         | 2.27        | 1.48       | 0.5      | 6          | 4             | 1.0                   | 54%               |
| MSI 11| 0.37         | 2.25        | 1.47       | 0.5      | 6          | 4             | 0.9                   | 60%               |
| MSI 12| 0.37         | 1.16        | 1.46       | 0.5      | 6          | 4             | 0.8                   | 54%               |
| MSI 13| 0.37         | 1.12        | 1.43       | 0.5      | 6          | 4             | 0.8                   | 54%               |