Incorporation of Polyoxometalates into Polymers to Create Linear Poly(polyoxometalate)s with Catalytic Function

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S Supporting Information

ABSTRACT: Organic polymers have been found widespread commercial applications due to their easy processing and attractive mechanical properties. Concurrently, inorganic polyoxometalates (POMs), a class of metal–oxygen anionic and nanosized clusters of early transition metals, have a wide range of attractive functions and are used in industrial catalysis. In this communication, we report a new approach to creating the first linear poly(polyoxometalate)s that combine the advantages of polymers and POM clusters. In the experiment, a POM-containing norbornene monomer was first synthesized by linking a Wells-Dawson-type POM with a norbornene derivative. The monomer was polymerized in the presence of a Grubbs catalyst under mild conditions with yields nearly 100%

in a living and controllable manner. The resulting poly(polyoxometalate)s have controllable molecular weights and a well-defined hybrid structure of an organic polynorbornene backbone with large pendant groups of the nanosized POM clusters. Thus, they form good films and have a good catalytic performance. Our findings not only pave the way for incorporating the POM clusters into polymers with well-defined structures and high molecular weights, but also offer a competitive strategy for developing more novel catalytic systems by introducing the poly(polyoxometalate)s.
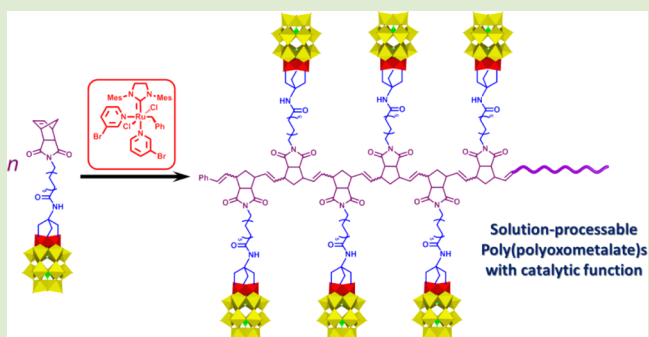
C lusters are fascinating ensembles of bound atoms intermediate in size between a molecule and a bulk solid.[1] They mainly contain the following classes: atomic or molecular clusters and robust clusters of transition metals and main group elements. These species are featured by large but definite physical structures and sizes, and diverse and complex chemical structures and compositions, thus, have unique and attractive properties and functions. However, cluster-containing polymers receive far less attention because of the synthetic difficulties.[2] The major obstacles are the steric effects due to their large size that may impede polymerization of cluster-containing monomers as well as chemical activity that may lead to undesirable side reactions. Thus, these polymers have low molecular weights, are insoluble, and have been poorly characterized.

Polyoxometalates (POMs) are a class of metal–oxygen anionic and nanosized clusters of early transition metals.[3] Their enormous structural and chemical diversity generates many attractive functions that have promoted a range of significant applications. For instance, they are excellent catalysts that have been widely used in industry.[4] The integration of POMs into polymer matrices may be a good method to creating novel POM-containing polymers possessing the unique properties of

POM clusters and the favorable processability of polymers.[5−7] So far, these polymers that are prepared through polymerization protocols of POM-containing monomers are insoluble in most solvents and thus are poorly characterized.

Living ring-opening metathesis polymerization (ROMP) has become a particularly powerful method for the synthesis of well-defined polymers, with accurate molecular weight control, low polydispersity, and complex polymeric architectures.[8] Because norbornene monomers can be easily functionalized by large and chemically active organic or inorganic moieties, many functional polynorbornenes bearing diverse side chains have been generated.[9] Thus, ROMP is also a robust synthetic strategy for the preparation of functional polymers.

In this Communication, we report for the first time, to the best of our knowledge, a new synthetic strategy for incorporating polyoxometalate clusters into polymers to generate linear poly(polyoxometalate)s, denoted as L-Poly-(POM)s, fully exploiting the advantage of living ROMP. In the experiment, a POM-containing norbornene monomer was first

synthesized and then polymerized when catalyzed by a Grubbs catalyst under mild conditions with high yields (nearly 100%) and in a living and controlled manner. The L-Poly(POM)s obtained, thus, have well-controlled molecular weights, low polydispersity, and a well-defined hybrid structure. Importantly, they can be processed in solution like conventional polymers and also demonstrate the catalytic performance of the POM cluster.

Scheme 1A shows the synthetic route of the designed POM-cluster containing norbornene monomer and polynorbornenes.

Scheme 1. (A) Synthetic Route of the POM-Containing Monomer and Polymers and (B) Schematic Picture of a Three-Dimensional Structure of the Hybrid Polymer[a]
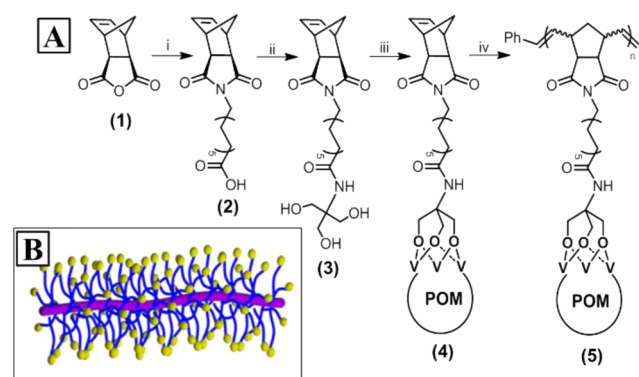

[a]Reagents and conditions: (i) 12-aminolauric acid, AcOH, 120 °C, 6 h; (ii) tris(hydroxymethyl) aminomethane, EEDQ, ACN, 85 °C, 24 h; (iii) [(n-Bu)$_4$N]$^+$$_6H_3P_2V_3W_{15}O_{62}$, DMF, 85 °C, 5 days; (iv) [(H$_2$IMes)(3-Br-py)$_2$(Cl)$_2$Ru=CHPh], DMF, rt, 2 h.

The POM cluster without counterions has an ellipsoidal shape with a long axis of 1.2 nm and a short axis of 1.0 nm,[10] and the repeating unit length of the polynorbornenes is in the range of 0.5−0.6 nm (Figure S1).[11] This difference in size may cause a steric hindrance along the polynorbornene backbone bearing the POM cluster pendants that obstructs the formation of the L-Poly(POM)s. Thus, we inserted a 12-carbon spacer between the norbornene moiety and the cluster. The monomer was synthesized via the following steps: (i) Linking *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride **1** with 12-amino-lauric acid generates the compound **2** with a carboxylic acid at the one end;[12] (ii) Further coupling **2** with tris-(hydroxymethyl)-aminomethane (denoted as Tris) via an amidation produces the compound **3** with three hydroxyl groups at the other end; (iii) Finally the norbornene monomer **4** was synthesized by combining **3** with the trivanadium-substituted Wells-Dawson-type polyoxotungstate [(Bu$_4$N$^+$)$_6$H$_3$(P$_2$W$_{15}$V$_3$O$_{62}$)$^{9−}$] through an esterification reaction between the three hydroxyls in **3** and trivanadium in the cluster.[14] Hereafter, the monomer is denoted as Mono-POM. Importantly, the cluster is encapsulated by six cationic tetrabutylammoniums (Bu$_4$N$^+$), so the reaction can be performed in DMF. The polymerization of the monomer in the presence of a third-generation Grubbs catalyst (ruthenium *N*-heterocyclic carbine, denoted as G3) was carried out in dry DMF under open air conditions at room temperature with extremely high yields (nearly 100%) in 2 h. Note that the calculated POM content of the Mono-POM is 68.0%. Since the molecular weight of the monomer is the same as that of the

repeating unit of the L-Poly(POM)s, the POM content of the polymers is also 68.0%.

Four L-Poly(POM)s **5** with different degrees of polymerization (DP) were prepared by controlling the molar ratio [M]/[G3] of the monomer and G3 catalyst. They are denoted as L-Poly(POM)$_n$ in which *n* is the expected DP$_{Theo}$. In this work, *n* = 10, 20, 50, and 100. Note that the L-Poly(POM)s have a well-defined hybrid structure: An organic polynorbornene backbone bearing large pendant groups of the nanosized POM clusters (Scheme 1B).

The monomer and polymers were carefully characterized, and the results are summarized in Figures S2−22 of the Supporting Information. In Figure 1 we highlight the important
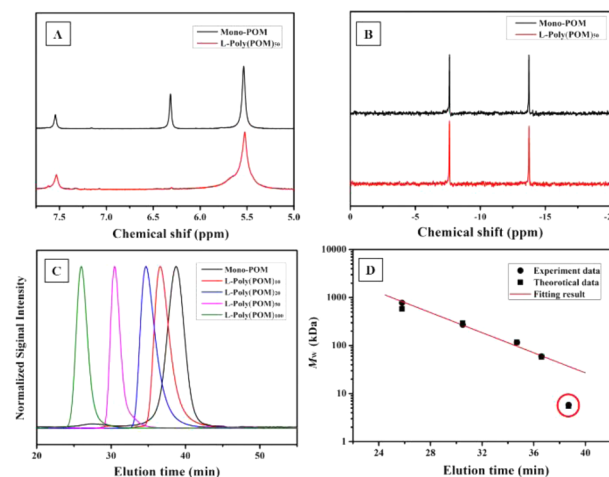
Figure 1. (A) Highlighted ^{1}H NMR spectra of Mono-POM and L-Poly(POM)$_{50}$ in DMSO-d_6. (B) ^{31}P NMR spectra of Mono-POM and L-Poly(POM)$_{50}$ in DMSO-d_6. (C) SEC traces of the Mono-POM and four hybrid polymers. (D) Semilogarithmic plot of the measured and theoretical molecular weights versus elution time. The solid line is the linear fitting result with R = 0.9889.

data that confirms generation of Poly(POM)s. The full ^{1}H NMR spectra of the monomer and the four polymers can be found in the Supporting Information. Figure 1A shows the ^{1}H NMR spectra of Mono-POM and L-Poly(POM)$_{50}$ in the chemical shift range of 5.00 to 7.75 ppm. The ^{1}H NMR spectrum of Mono-POM shows three signals at δ = 7.53, 6.30, and 5.52 ppm with an intensity ratio of 1/2/6. They correspond to one amide proton, two vinyl protons and six tris-methylene protons. Clearly, the vinyl protons at δ = 6.30 ppm disappear after polymerization (Figure 1B). For polynorbornenes, there are normally two new vinyl protons that appear as a broad signal at approximately δ = 5.40 and 5.60 ppm corresponding to the *cis*- and *trans*-conformations of the double bonds of the polymer backbone. Unfortunately, for L-Poly(POM)s they were overlapped with the methylene protons of Tris at δ = 5.52 ppm by coincidence. However, careful observation shows two shoulder peaks appearing around at δ = 5.45 and 5.65 ppm. The integral area of the peak(s) from δ = 5.2 to 5.9 ppm is about 8 larger than that of the peak at δ = 7.53 ppm (Figure S18). These ^{1}H NMR data indicate an almost complete norbornene-to-polynorbornene conversion.

Figure 1B is the ^{31}P NMR spectra of Mono-POM and L-Poly(POM)$_{50}$. The two signals at δ = −7.63 and −13.74 ppm correspond to the two phosphorus heteroatoms residing at different positions of the POM cluster.[13] Meanwhile, the IR

characterization of the four hybrid polymers exhibits infrared signals at ν = 1086, 955, 912, and 822 cm^{-1} (Figure S22).[13] They are the characteristic signals of the POM cluster. The ^{31}P NMR and IR evidence indicate intactness of the POM cluster in the L-Poly(POM)s.

The molecular weight and polydispersity of the L-Poly-(POM)s were further characterized using size-exclusion chromatography (SEC). Note that the instrument was equipped with both refractive index and online light-scattering detectors. The normalized SEC traces in Figure 1C display monomodal molecular weight distributions of the monomer and four polymers. The online light-scattering detector provides the absolute molecular weights ($M_{w,SEC}$) of the L-Poly(POM)s with the special macromolecular architecture (Scheme 1B). Table 1 summarizes the molecular weights and

Table 1. Molar Ratios, Molecular Weights, and Polydispersities of the Monomer and Hybrid Polymers

samples	[M]/[G3]	$M_{n,Theo}$ (kDa)	$M_{w,SEC}$ (kDa)	PDI
Mono-POM		5.8	5.5	1.16
L-Poly(POM)$_{10}$	10/1	58.3	59.4	1.09
L-Poly(POM)$_{20}$	20/1	116.7	116.7	1.07
L-Poly(POM)$_{50}$	50/1	291.6	270.9	1.15
L-Poly(POM)$_{100}$	100/1	583.3	774.9	1.15

polydispersities of the monomer and the four polymers prepared at the different molar ratios [M]/[G3]. The theoretical molecular weight, $M_{n,Theo}$ is calculated directly from [M]/[G3] used before polymerization. The relatively small difference between $M_{n,Theo}$ and $M_{n\ SEC}$ indicates again an almost complete monomer-to-polymer conversion. The small polydispersity indexes (PDI) indicate that the well-controlled characteristics of ROMP were retained for the polymerization. Figure 1D shows a semilogarithmic plot of the measured and theoretical molecular weights versus elution time. A good linear relation in this semilogarithmic scale indicates that these L-Poly(POM)s exhibit a feature of the coiled polymer chain in the dilute solution. Therefore, the L-Poly(POM)s can behave, to some extent, like most conventional polymers.[14] Notably, the measured data of the hybrid monomer is not in this line, as marked by the red circle. It is reasonable that the hybrid monomer does not have the feature of the coiled polymer chain. Here, we can conclude that our success in the synthesis of the L-Poly(POM)s with well-defined structures and molecular weights clearly demonstrates that the large size and special chemical activity of the POM cluster do not impede polymerization of the POM-containing monomer and/or lead to undesirable side reactions.

Normally, almost pure inorganic POM clusters in crystalline or powder form are difficult to process limiting their further applications in materials science. However, the L-Poly(POM)s can be processed from solutions to form thin films. Two TEM images in Figure 2 display the morphology of a thin film sample of L-Poly(POM)$_{50}$ prepared by a casting process from its dilute acetonitrile solution. The low-magnification image in Figure 2A shows homogeneous morphology indicating a good film-forming ability, whereas the high-magnification image in Figure 2B displays an inhomogeneous morphology, including dark dots with a diameter of about 2 nm and some dark wormlike threads with a length of about 5 nm and a width of 2 nm. The inhomogeneity reflects the characteristics of the hybrid structure that exists in the condensed film. This good film-
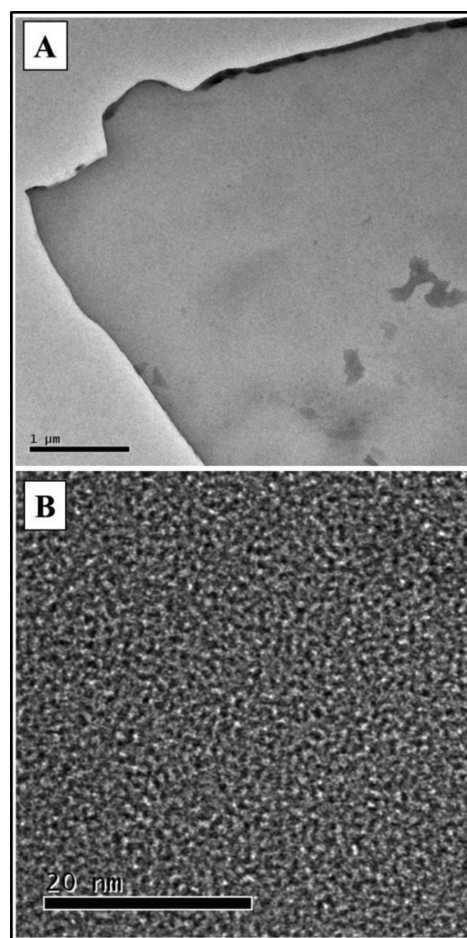
Figure 2. TEM images of a thin film of L-PolyPOM$_{50}$ prepared by the casting process of an acetonitrile solution. Images (A) and (B) obtained at different magnifications shows homogeneous and inhomogeneous morphologies.

forming ability leads us to conclude that the L-Poly(POM)s are solution-processable, very differently than pure POM clusters.

The catalytic function of the L-Poly(POM)s was appraised via the oxidation of the sulfide, tetrahydrothiophene (THT).[13b,15] The THT was oxidized into tetrahydrothiophene oxide (THTO) by H_2O_2 in the presence of the monomer or the L-Poly(POM)s in acetonitrile at room temperature. Figure 3A shows the time course of H_2O_2 oxidations and control reactions. Over 95% THT was converted to THTO in 90 min and no sulfone was observed. The catalytic reactivity decreased in the order: L-Poly(POM)$_{10}$ > L-Poly(POM)$_{20}$ ≈ L-Poly-(POM)$_{50}$ > Mono-POM ≈ L-Poly(POM)$_{100}$. It is difficult to explain this finding at present. Probably, the catalytic activity of some POM clusters is reduced due to the polymer chain coils in the dilute solution. Control experiments showed that no reaction took place without using either POMs or H_2O_2. This unambiguously demonstrates that the L-Poly(POM)s still have the catalytic function of the POM cluster. This brings a new concern whether the catalytic activity of the POM cluster wound or even destroy the organic backbone. To this end, we performed measurements of the molecular weights of the recycled L-Poly(POM)$_{50}$ and L-Poly(POM)$_{100}$ samples after the THT catalytic oxidation using the SEC method. In Figure 3B the SEC traces of the recycled samples are compared with those of the original samples of the L-Poly(POM)$_{50}$ and L-
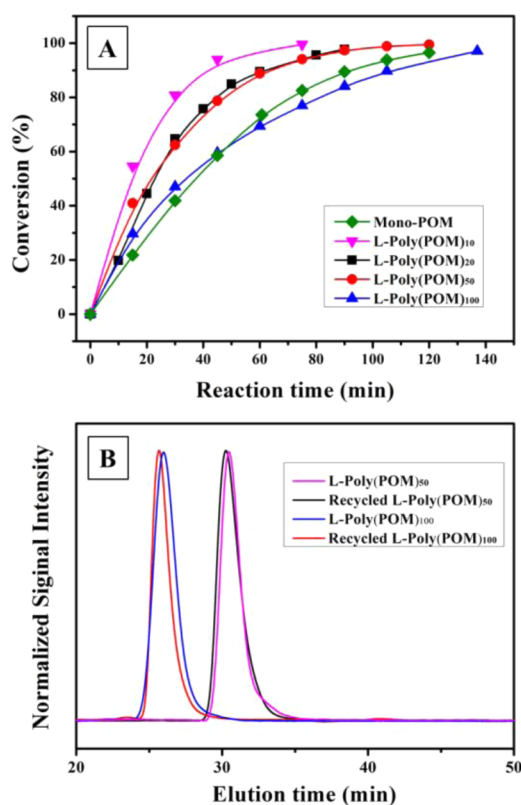
Figure 3. (A) Conversion of tetrahydrothiophene oxide (THTO) in the oxidation of tetrahydrothiophene (THT) catalyzed by Mono-POM and L-Poly(POM)s. (B) SEC traces of the L-Poly(POM)$_{50}$ and L-Poly(POM)$_{100}$ before and after the THT catalytic oxidation.

Poly(POM)$_{100}$. The small differences between the SEC traces for the same L-Poly(POM)s indicate a nearly identical molecular weight for the original and recycled samples. This finding further means no detectable degradation of L-Poly(POM)s occurred during the THT catalytic oxidation. Significantly, these recycled samples could be reused without loss in catalytic activity.

In summary, we have successfully incorporated a POM cluster into a polymer to create well-defined linear poly-(polyoxometalate)s with high molecular weights and low polydispersities by utilizing a robust living ROMP strategy. This success further indicates that the steric hindrance and special chemical activity of the POM cluster do not impede polymerization of the POM-containing monomer and/or lead to undesirable side reactions. The product has a well-defined hybrid structure, that is, an organic polynorbornene backbone bearing large pendant groups of the nanosized POM clusters. The poly(polyoxometalate)s combines the processability of conventional polymers and the functions of POM clusters. The advantages were used to prepare solution-processed thin films and to catalyze the oxidation of a sulfide, respectively. Studies on their applications in electrode modification, electrocatalysis, and photochromic and electrochromic devices are ongoing. Meanwhile, this polymerization method is also being utilized for the preparation of poly(polyoxometalate)-polymer block copolymers and hybrid nano-objects.

ASSOCIATED CONTENT

S **Supporting Information**

Experimental section; ^{1}H and ^{13}C NMR, ^{31}P NMR, FT-IR, and MS/ESI spectra of the precursors, monomer, and poly-(polyoxometalete)s; EDX spectra and TEM images of the poly(polyoxometalete)s, HPLC spectra of the catalytic oxidation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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