Metallopolymers from organically modified polyoxometalates (MOMPs): A review

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ABSTRACT

Metal-containing monomers are the building blocks for metallopolymers, and play very important role in their functions. As a class of new building block, the incorporation of organically modified polyoxometalates (OMPs) to metallopolymers not only broaden the kind of metal elements in metallopolymers, but also introduce novel functions. Herein, a survey of the progress in the OMPs-based metallopolymers is given. The organic modification methods of OMPs, synthetic strategy of OMPs-based metallopolymers, as well as their applications will be discussed.

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1. Introduction

Metallopolymers received broad attentions due to their multiple applications in catalysis, optics, electrochemistry, magnetics, as well as biomedicine [1–5]. In most cases, the functions of metallopolymers mainly rely on the metal-containing building blocks [6–9]. Development of new building block and functions are still research focus for the novel metallopolymers. Polyoxometalates (POMs), a kind of inorganic cluster, which can incorporate more than 70 different kinds of metal elements into their frameworks, are widely used in both fundamental research and industrial applications [10–12]. Basically, there are mainly two different
strategies to introduce POMs into polymeric system [13–16]: (i) electrostatic interaction between positive charged monomer followed by further polymerization or direct interaction with positive charged polymer; (ii) organically modification of POMs with potential polymerizable groups, such as coordination site, hydrogen-bonding pair, and vinyl groups. Some pioneers in this area already summarized the progress of both strategies, some recent review articles are suggested [17–21]. In this contribution, we will only focus the recent progress on metallopolymers with organically modified POMs as building block, especially their synthesis, as well as potential applications. Normally, the organically modified POMs (OMPs) can be derived from lacunary POMs through different reactions with organic precursors, such as esterification, silanization, imidoylation and so on. Fig. 1 shows the structure of four kinds of POMs that are frequently used in the preparation of metallopolymers from organically modified polyoxometalates (MOMPs).

In terms of the topology of the resulted metallopolymers, OMPs-based metallopolymers can be divided into the following five different kinds (as shown in Scheme 1): (i) side chain, in which the OMPs building blocks are on the side chain of the polymer; (ii) main chain, where the OMPs building blocks are incorporated in the backbone of the polymer, which can be further divided into OMPs-terminated polymers and OMPs main chain polymers; (iii) network, where OMPs act as node of the network; (iv) dendrimer or dendron, where the OMPs are on the periphery of either the dendrimer or dendron; (v) metallomacrocycles, where OMPs are on the node of the macrocycles. According to the driving force to build MOMPs, there are two ways: covalent bond, such as free radical polymerization, controlled polymerization, as well as post-modification of polymer precursor; non-covalent bond, such as ligand-metal coordination, hydrogen-bonding, host-guest interaction, and photo dimerization. In the following section, we will summarized progress of MOMPs according to their topologies. For the clearance, all the counterions of POMs were neglected in the structures, only their cluster structures were shown.

2. Observation and discussion

2.1. Side chain

Direct polymerization of vinyl group-modified POMs via conventional free radical way is the first and easiest way to prepare side chain MOMPs. To the best of our knowledge, Judeinstein reported the first so-called side chain MOMPs [22]. As shown in Fig. 2, a series of trichlorosilane-modified OMPs (1 for example) with polymerizable groups were synthesized, which can further undergo free radical polymerization initiated by benzoyl peroxide (BPO) or azodiisobutyronitrile (AIBN). Since they used difunctionalized OMPs as monomer, as they mentioned, topologies such as linear, branched, even network were observed. As a pioneering research in the field of MOMPs, this work is a milestone in the development of MOMPs and established the strategy of polymerization of OMPs.

Obviously, mono-substituted OMPs monomers are essential to prepare real side chain MOMPs. As shown in Fig. 3, there are mainly two kinds of such kind of monomers: (i) organoimido-modified Lindqvist type [Mo₆O₁₉]²⁻; (ii) trioxo-modified Dawson type [P₂V₃W₁₅O₆₂]²⁻.

As shown in Fig. 3A, Maatta group prepared styryl monosubstituted OMP monomer 2. Further copolymerization with 4-methyl-styrene at 60 °C for 48 h gave the side-chain MOMPs, which was proved by both FT-IR and ¹H NMR [23]. However, no information about molecular weight was reported.

Similarly, Peng group also used the imidoylation strategy to prepare OMP monomers with two ethynyl groups [24], as shown in Fig. 4. These ethynyl modified OMP can undergo Sonogashira coupling polymerization catalyzed by Pd[PPh₃]₂Cl₂ and Cul to give
conjugated polymers 4 and 5 with OMPs as pendants. The molecular weight was tentatively characterized by gel permeation chromatography (GPC). With light scattering detector, it was found that the molecular weight of these MOMPs can achieve 15.7 kg/mol. These side chain MOMPs exhibited fluorescence emission around 480 nm, while the fluorescence intensities and quantum yields of these MOMPs were significantly lower than that of the conjugated polymer without POMs pendants. It is believed that the side chain POMs pendants linked through conjugated bridges in 4 exhibited a much higher fluorescence quenching effect than those with flexible alkyl bridges in 5, indicating that the through-bond photo induced electron transfer may be the dominant mechanism for fluorescence quenching. It was found that these MOMPs could form reverse vesicles in nonpolar solvent such as toluene due to the amphiphilic characteristics, and form tubular structures in polar solvent such as DMSO due to polyelectrolyte properties [25].

Obviously, direct polymerization of OMPs monomers through free radical method lost the control over the structure of resulted MOMPs. In order to better control the polymerization process and the functionalities of the resulted MOMPs, Peng group also investigated the post-modification of precursor polymers. For example, they synthesized a diblock MOMP in the following way [26]: as shown in Fig. 5, precursor polymer with amine group protected by phthalic anhydride was firstly synthesized through atom transfer radical polymerization (ATRP), followed by subsequent conversion of the end group to azide, then clicked with alkynyl-terminated oligo(phenylene vinylene) (OPV). After removing the phthalimide protection groups in the coil block to give free aryl amines, [Mo6O19]2− clusters were finally attached to the coil block covalently to yield the diblock MOMPs 6. The resulted polymer showed good solubility in normal organic solvent, such as chloroform, THF and so on. Therefore, the successful synthesis can be confirmed by the complete and continuous GPC peak shift after each step. However, due to the steric hindrance, post-modification of the

**Fig. 4.** Structure of side chain MOMPs based on imidoylation of [Mo6O19]2−. Reproduced from ref. 24. with permission from Copyright (2005) American Chemical Society.

**Fig. 5.** Synthetic procedure for side chain MOMPs 6 and 7 by post-modification.
precursor with POMs cannot guarantee 100% efficiency. In consistent with previous conjugated MOMPs, these hybrid polymers showed little fluorescence quenching in solution. While the POM cluster was found to quench 74% of the OPV fluorescence in films, which was likely due to a photo induced electron-transfer process from the OPV donor to the POM cluster, making it a potential candidate as an efficient photovoltaic material.

Similar diblock MOMPs 7 with poly(3-hexylthiophene-2,5-diyl) (P3HT) instead of OPV was also synthesized by Peng group (as shown in Fig. 5) [27]. Compared with OPV, P3HT show much higher tendency of microphase separation. After cluster attachment, the hybrid diblock copolymers showed much less solvent and size dependence in phase-separated morphologies of their pristine films. The sporadic and isolated conducting domains seen in the pristine films changed to widespread worm-like conducting networks after thermal annealing; such morphologies were conductive to photovoltaic properties. Single-component photovoltaic cells of MOMPs 7 and inverted solar cells on ZnO nanorod arrays/7 were fabricated, showing power conversion efficiencies only up to 0.055% [28]. In these diblock copolymers, POMs block was hydrophilic and the P3HT block was hydrophobic. Driven by solvophobic-solvophilic interactions, they were able to form hollow spherical vesicular structures in solution [29].

As mentioned in Fig. 3B, Dawson type [P2V3W15O62]6– is another type of POMs which can be used to prepare monosubstituted OMPs. The modification of [P2V3W15O62]6– involves an esterification between tris-hydroxyl and terminal oxygen atoms from POMs. By reacting tris(hydroxymethyl)aminomethane (Tris)-modified [P2V3W15O62]6– with methacryloyl chloride, Pradeep and coworkers synthesized the OMP monomer 8 (Fig. 6) [30]. Copolymerization with (methacryloyloxy)phenyldimethylsulfonium triflate (MAPDST) and methylmethacrylate (MMA) gave the resulted MOMPs 9 and 10 as brownish yellow solid, with good solubility in organic solvent, such as acetonitrile, DMF, and dichloromethane at room temperature. Preliminary tests indicated that these MOMPs showed good photoresistance towards electron beam (E-beam)/ extreme ultraviolet (EUV), especially the MOMPs 9 with MAPDST, due to the efficient photon harvesting by the POM clusters from the EUV source.

Although free radical polymerization shows its advantage in facile synthesis of MOMPs, while its disadvantage is the less control over molecular weight, polydispersity, as well as end group functionality. Wang group reported the first “living” polymerization of OMPs monomers [31]. As shown in Fig. 7, ring-opening metathesis polymerization (ROMP) of norbornene-modified OMPs monomer 11 catalyzed by Grubbs 3rd catalyst in DMF can prepare MOMPs with degree of polymerization of 100 within 2 h. The living characteristics of the polymerization can be proved by the linear kinetic plot and the narrow polydispersity. By using DMSO GPC with both refractive index and online light-scattering detectors, they measured the absolute molecular weight (M_wSEC) of MOMP 12 for the first time. As expected, the experimental M_w by GPC matched well with the theoretical M_w, calculated by the monomer conversion. These MOMPs can form a homogeneous film by simple casting. Chain extension to 6-norbornene-hexanoic acid gave well-defined diblock copolymer 13 with different block ratios [32]. The introduction of the second block not only adjusted the amphiphlicity of the MOMPs, but also greatly improved their processability. For example, MOMPs with block ratio of poly(POM)_{35}-b-poly(-COOH)_{232} can form spherical micelles in acetonitrile, which further packed into hexagonal pattern to form a film. By adjusting the block ratio, one can easily tune the organic content in the MOMPs, which may further improved their processability. In the case of organic content of 65.6% (that is poly(POM)_{35}-b-poly(COOH)_{100}), the casting film of MOMPs was not brittle any more, can even be bended by a tweezer [33]. The presence of [P2V3W15O62]6– also endowed these MOMPs with catalytic activities towards oxidation of sulfur-containing compounds.

Polymerase chain reaction (PCR) can also be used to prepare side-chain MOMPs [34]. Hasenknopf and coworker synthesized a series of POMs-deoxynucleotide (POM−dNTP) bioconjugates linked through 7-deaza-modified purines, which is polymerase-
compatible and can be used in PCR amplification of DNA. The multiple redox chemistry of the POM cluster endowed the MOMP with electrochemistry properties and can be used in the detection of bio-warfare agent, such as *Yersinia pestis*.

2.2. Main chain

Based on the position of OMPs building blocks on the main chain, there are three different types of main chain MOMPs: (i) OMPs as repeat unit in the backbone of MOMPs, which can be synthesized through hydrogen bonding, ligand-metal coordination, C–C coupling of di-functionalized OMPs; (ii) OMPs as initiator at one end of MOMPs, which were normally synthesized by controlled radical polymerization methods, such as reversible addition–fragmentation chain transfer (RAFT), ATRP; (iii) OMPs in the middle of MOMPs, which were synthesized either from di-functionalized OMPs initiator or post-modification of di-functionalized OMPs.

2.2.1. OMPs as repeat unit in the backbone of MOMPs

Lu and coworkers synthesized OMPs-containing polyimide through copolymerization of bis-aminol-functioned OMP 14 with pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) (Fig. 8)[35]. The incorporation of OMPs in the main chain of MOMP 15 not only improve the thermal and mechanical properties of the polymer films, but also fabricate a polyimide hybrid film with ultralow dielectric constant ($\kappa = 1.22$). It is believed that the heterostructure of the film and the induced variations in the polarization effect and binding energy play important roles in the prominent decreasing of $\kappa$.

One important building block used in the preparation of such...
kind of main-chain MOMPs is symmetrically modified Anderson-type \([\text{MnMo}_6\text{O}_{18}]^{3-}\) cluster. Hasenknopf and coworkers reported the first example of main chain MOMPs based on coordination between pyridine-symmetrically modified OMP coordinated with PdCl\(_2\)(PhCN)\(_2\) (Fig. 9A) [36]. The coordination was achieved by simply mixing the two building blocks and was monitored by \(^1\text{H} \) NMR. A transparent and birefringent gel was formed after addition of specific solvents, such as methanol. It was found that the concentration of the OMPs were also very important in this case.

Similarly, by grafting base pair, such as adenine and thymine, symmetrically on \([\text{MnMo}_6\text{O}_{18}]^{3-}\) cluster, Wu group reported a supramolecular polymer 19 based on hydrogen bonding [37] (Fig. 9B). The driving force was identified by \(^1\text{H} \) NMR and the formation of such supramolecular MOMP was also visualized by the increasing of specific viscosity, which allow the process of such MOMPs. Further cross-link of this supramolecular MOMP with dicatonic surfactant through electrostatic interaction yield a network gel. Cronin group synthesized a Strandberg-type \([\text{Mo}_5\text{O}_{15}]^{2-}\) cluster 20 with guanosine symmetrically modified (Fig. 9C). Interestingly, driven by the intermolecular hydrogen bonding, this OMP can form double helix structure that nearly identical to Z-type DNA [38]. The chiral structure was kept in solution as demonstrated by corresponding temperature-dependent circular dichroism spectra as well as AFM images on mica. As expected, this OMP formed the first example of polyoxometalate-containing hydrogel even at concentration as low as 1.28 wt%.

Photo dimerization was also introduced in the preparation of main chain MOMPs. Song group grafted photo active coumarin on each side of \([\text{MnMo}_6\text{O}_{18}]^{3-}\) cluster to generate OMP 21 [39]. Taking advantage of the reversible photo dimerization and dedimerization, they were able to prepare main chain MOMP 22 as shown in Fig. 10. The formation of MOMP was proved by GPC, which gave the relative molecular weight of such MOMP as 337.38 kDa with polydispersity of 1.60. A significant color change from light-yellow to deep-brown was observed during the photo-dimerization, which perhaps originated from the synergistic interaction between coumarin group and \([\text{MnMo}_6\text{O}_{18}]^{3-}\) cluster. This reversible color change was accompanied by the reversible luminescent change, which may be used in display.

**Fig. 10.** Photo dimerization induced the preparation of MOMP 22. Reproduced from ref. 39, with permission from Copyright (2014) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
One drawback in the preparation of main chain MOMPs is the poor control over the polymerization due to simultaneous chain growth. Cronin group reported a stepwise growth approach to build MOMPs through Cu-catalyzed alkyne–azide cycloaddition (CuAAC) [40]. As shown in Fig. 11, four different OMPs monomers with azide (or alkyne) groups symmetrically and mono-modified MnMo6 cluster were synthesized. Subsequent coupling reactions between these mono- and di-functioned OMPs gave mono-dispersed linear MOMPs oligomers (2–5 clusters), allowing precise control over the size and structure of the resulting MOMPs. The preparation of MOMPs can be identified by corresponding ion mobility spectroscopy–mass spectroscopy (IMS-MS) (Fig. 11B). Definitely, repeated addition and click reaction can produce main chain MOMPs with pre-determined molecular weight and compositions. However, a much easier coupling reaction or polymerization approach was needed in order to realize practical preparation of such main chain MOMPs.

\[
\text{[Mo}_8\text{O}_{19}\text{]}^{2-} \text{ is another important building block to prepare main chain MOMPs which was initially developed by Peng group. As shown in Fig. 12A, di-functionalized [Mo}_8\text{O}_{19}\text{]}^{2-} \text{ monomers (30 and 31) with either iodobenzene [41] or ethynylbenzene [42] can be prepared through the imidoylation between [x-Mo}_8\text{O}_{26}\text{]}^{6-} \text{ cluster and corresponding aromatic amines catalyzed by N,N'-dicyclohexyl methanediamine (DCC). Subsequent Sonogashira coupling of these monomers with 2,5-di(2,2-dimethylpropoxy-1,4-diethynylbenzene) or 2,5-di(2,2-dimethylpropoxy-1,4-diiodobenzene) gave the conjugated main-chain MOMPs (32) (Fig. 12B). It should be noted that the Mo–N bond in the monomer is not very stable toward excess amount of triethyamine (TEA). To avoid the decomposition of monomers and keep the higher polymerization rate, a mixture of 1 equiv. of TEA and excess K2CO3 was found to be the best base in the reaction.}
\]

The resulted main-chain MOMPs can dissolve in polar solvents, such as DMF and DMSO, allowing preparation of free-standing films through spin-coating or solution casting. Solution study indicated that these MOMPs preferred a stretched or extended conformation in good solvent. Addition of poor solvent induced the formation of hollow cylindrical structures, which was driven by counterion induced attractions [43]. Similar to their counterpart of the side chain MOMPs [26], these conjugated main chain MOMPs show intense absorption in the visible range and with little fluorescence emissions. Simple single-layer photovoltaic (PV) cells with a device configuration of indium-tin oxide (ITO)/polymer/Ca/Al was fabricated and gave a power conversion efficiency of 0.15%, which is significantly higher than PV cells fabricated with other conjugated polymers in the same device configuration. The power conversion efficiency can be further improved to 0.24% by introducing polythiophenes into the conjugated structure (Fig. 12C) [44]. The polythiophenes-containing MOMP 33 was synthesized through Stille coupling reaction between iodobenzene-modified OMP 30 and 2,5-bis tributylstannyl)-thiophene.

### 2.2.2. OMPs as initiator at one end of MOMPs

To synthesize OMPs capped MOMPs, one facile way is to use mono-functioned OMPs as initiator or polymerization agent. The most frequently used mono-substituted cluster in this case is the Dawson type [P2W17O61]10– and [P2W15V3O62]9– cluster. Wang group reported the first example of OMPs capped MOMPs. In detail, they modified the [P2W17O61]10– cluster with an ATRP initiator, which was then used in conventional ATRP process of styrene (Fig. 13A) [45]. Kinetic study indicated the “living”/controlled characteristics of the ATRP process, the resulted MOMP 35 showed a well-defined structure as demonstrated by the narrow polydispersity index. The counterion tetrabutyl ammonium (TBAs) can be facilely exchanged by using Dowex H⁺-50W-X2 resin, which was confirmed by the turbidity change. Such an exchange process changed the amphiphilicity, resulting an amphiphile with giant headgroup. It was found that once the giant hybrid amphiphiles formed, they immediately assembled into kinetically favored vesicular aggregates. During subsequent annealing these vesicular aggregates were transformed into thermodynamically stable vesicular aggregates with a perfect vesicle structure [46]. A further thermal treatment induced an evolution from vesicles to tubular aggregates, in which H⁺–POM formed the nanotubes and wrapped with PS.
To tune the amphiphilicity and self-assembled structure of these MOMPs, an amphiphilic poly(ethylene glycol) (PEG) chain was connected to \([\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]^{13-}\) cluster through covalent bond (Fig. 13B) [48]. The synthesis started from mono-hydroxyl PEG, followed by subsequent esterification with succinic anhydride and amidation with Tris to yield trihydroxyl-terminated PEG, which was finally reacted with \([\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]^{13-}\) to give the target MOMP 36. As expected, the immiscibility between POMs and PEG chain resulted in a microphase separation to form POM and PEG layers, which further arranged into hybrid lamellae with a sub-20 nm thickness. These hybrid lamellae simultaneously organize into spherulitic superstructures, which were stable at temperature as high as 160 °C. Given by the immiscibility of OMPs with PEG and the miscibility of PEG themselves, by mixing PEG-containing MOMPs with PEG, they observed four nanostructures in the solid samples of nanocomposites: hybrid self-assembled nanosheets, PEG crystallized lamellae, PEG/hybrid cocrystallized lamellae, and hybrid crystallized lamellae [49]. The PEG-modified MOMPs was found to be a nanoenhancer to tune the properties, for example, the shear storage modulus of the nanocomposites increased by many orders of magnitude at temperature above the melting point of the PEG matrix.

Similarly, poly(ε-caprolactone) (PCL) with different molecular weights were also grafted to \([\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]^{13-}\) (Fig. 13C) [50]. Taking advantage of the molecular weight-dependent self-assembly of these PCL-modified MOMP 37, both nanosheets and nanotubes can be achieved by adding water to the DMF solution. It is believed that the molecular weight dependent crystallinity of PCL played very important role in the formation of these structures. The nanosheets can be also used as nuclei to initiate the growth of nanotubes, which finally gave much complex tube-graft-sheet nano-objects (Fig. 14).

\[\text{a}_1-\text{[P}_2\text{W}_{17}\text{O}_{61}]^{10-}\] are another kinds of widely used cluster to prepare main chain MOMPs. This strategy was developed by Hasenkopf and Lacôte, including post-modification and direct polymerization (Fig. 14). In the case of post-modification approach, amino-terminated poly(N,N-diethylacrylamide) was first synthesized through RAFT polymerization, which was then reacted with mono-oxoacylated \[\text{a}_2-\text{[P}_2\text{W}_{17}\text{O}_{61}]^{10-}\] [51]. The successful preparation of MOMP 39 can be proved by corresponding GPC trace and \(^1\text{H}\) NMR. The thermoresponsive property of PDEAAm was changed from 43 °C for pure PDEAAm to 34 °C due to the presence of organically-modified POM in the MOMPs. By reacting amine-

Fig. 13. (A) ATRP preparation of MOMP 35; (B) and (C) preparation of MOMP 36, 37 by post-modification.

Fig. 14. TEM images and corresponding schematic illustration of the nanosheets and nanotube formed by MOMP 37, and the formation of tube-graft-sheet nano-objects. Reproduced from ref. 50. with permission from Copyright (2015) American Chemical Society.
terminated polypeptide with either mono-oxoacylated $\alpha_1$-and $\alpha_2$-[P$_2$W$_{17}$O$_{61}$]$^{10-}$, polypeptides-POMs MOMP 40 and 41 can be prepared [52]. They also synthesized the first example of POM-DNA conjugate 42 by reacting either mono-oxoacylated $\alpha_2$-[P$_2$W$_{17}$O$_{61}$]$^{10-}$-38 with amine-terminated DNA sequence [53]. However, there are some problems and limitations in this synthesis: (i) trithiocarbonate group has to be 100% removed because of its potential reaction with amine group; (ii) deprotection of the amine end group has to be 100% due to the difficulty in the purification of POMs-modified MOMPs and the protected polymer; (iii) efficient amidation between amine-terminated PDEAAm and mono-oxoacylated $\alpha_2$-[P$_2$W$_{17}$O$_{61}$]$^{10-}$.

Direct polymerization approach can avoid the above problems. As shown in Fig. 15B, OMP-based RAFT agent 44 was designed and synthesized through click reaction between ethynyl-terminated RAFT agent and azide-terminated $\alpha_1$-[P$_2$W$_{17}$O$_{61}$]$^{10-}$-43 [54]. RAFT polymerization of DEAAm with the aid of the POMs-based RAFT agent followed a controlled radical polymerization approach, as indicated by the linear kinetic plot of $M_n$ vs conversion and the narrow PDI. It should be noted that the polymerization rate was slower in the presence of POM than without POM, which may due to the possible redox process between POM and radicals. The photocatalytic activity of [P$_2$W$_{17}$O$_{61}$]$^{10-}$ was preserved in the resulted MOMP and can be used to prepare metal nanoparticle with long-term stability, where the polymer chain served as a stabilizer. The thermal responsiveness of the PDEAAm was also tuned due to the presence of POM [55]. They found that the aggregation mechanism at high temperature were different according to the amphiphilicity of counterions of POM. For example, in the case of hydrophobic TBA$s$, the transition was very sharp and the enthalpy was close to that of the purely polymer. While for the hydrophilic NH$_4^+$, the transition was prolonged and the enthalpy was smaller, indicating a change in the aggregation mechanisms presumably due to the enhanced stabilization by the hydrophilic POMs.

2.2.3. OMPs in the middle of MOMPs

For the synthesis of MOMPs with OMP in the middle of the polymer chain, di-functionalized OMPs were used. Wang group reported the first example of such kind of MOMP (Fig. 16A), Hydroxydifunctionalized [MnMo$_6$O$_{18}$]$^{3+}$-46 was used as initiator in the ring opening polymerization (ROP) of ɛ-caprolactone [56]. Direct initiation from the hydroxyl groups on OMPs in presence of Sn(OCT)$_2$ as catalyst failed, probably due to the electronegativity of the POM. By activating the hydroxyl groups with 4,4'-(dimethylaminomino) pyridine, the target PCL-OMP-PCL MOMP 47 was obtained. However, compared with ROP of ɛ-caprolactone, the preparation of PCL-OMP-PCL polymer was not in a well-controlled way, as the PDI was as broad as 1.56. Nevertheless, the introduction of POM covalently into PCL prevented the polymers from diffusing in melt and affected the crystallization process. To avoid the influence of POM in the polymerization, they also used the CuAAC reaction to graft PCL to Dawson type $\alpha_2$-[P$_2$W$_{17}$O$_{61}$]$^{10-}$-cluster (Fig. 16D) [57]. Due to the controlled preparation of PCL and subsequent quantitative grafting reaction, the GPC of resulted MOMP 54 gave PDI as low as 1.09.

Peptide chains can also be integrated with OMPs by either solution or solid phase approaches [58]. N-Hydroxysuccinimide (NHS) activated carboxylates symmetrically modified [MnMo$_6$O$_{18}$]$^{3+}$-51 (Fig. 16C) can be used to react with amino terminated polypeptides in the presence of N,N-diisopropylethylamine. As a conventional and powerful procedure, solid-phase peptide synthesis (SPPS) can also be used to prepare such kind of peptide-POM conjugates. By using asymmetrical modified [MnMo$_6$O$_{18}$]$^{3+}$-cluster with an activated C terminus and Fmoc-protected N terminus, MOMP with composition of H$_2$N-Val-Leu-MnMo$_6$-Ala-Val-Leu-Ala-OH was successfully synthesized as demonstrated by the corresponding electrospray ionization mass spectrum (ESI-MS).

In an attempt to study the potential application of MOMP in high density data storage, Zhang and coworkers synthesized a POM-containing polymer 50 by copolymerization of methyl acrylate symmetrically modified [MnMo$_6$O$_{18}$]$^{3+}$-49 with methyl methacrylate (Fig. 16B) [59]. They found that this kind of MOMP can realize a ternary resistance switching memory with good endurance and good retention. They ascribed the mechanism of the multilevel resistive switching property of this MOMP to the multiredox states of manganese center in the cluster, which can change the effective carrier density in the hybrid-polymer switching layer.

Fig. 15. (A) Post-modification to prepare main chain $\alpha_2$-[P$_2$W$_{17}$O$_{61}$]$^{10-}$-based MOMP 39, and the structure of other main chain MOMPs 40–42 with similar structures; (B) direct polymerization to prepare main chain MOMP 45 by RAFT process.
under an electric field.

2.3. Network

For the construction of network MOMPs, there are mainly five different approaches reported: (i) polymerization of multiple vinyl-modified OMPs, (ii) covalent organic framework (COF) from OMP-based building blocks, (iii) electrochemical polymerization of OMP monomers, (iv) metal coordination framework from OMP-based ligands, (v) host-guest complex between host-based polymer and guest modified OMPs.

As mentioned earlier, Judeinstein reported the first so-called side chain MOMPs [22]. However, since the OMP monomer used in their work were divinyl functionalized, a network structure was expected after free radical polymerization, which was also mentioned in their results. Therefore, to avoid the presence of linear polymer, multiple vinyl groups functionalized OMPs should be used and it’s better to use these di- or multi-vinyl functionalized OMPs as crosslinker to copolymerize with other monomers. Fig. 17 list some of the di- and multi-vinyl functionalized OMPs. Followed these strategies, Cabuil, Thouvenot, Lalot, and coworkers achieved the preparation of networked MOMPs by copolymerizing tetra vinyl functionalized OMP 55 with acrylamide [60,61]. The resulted MOMPs were hydrogel, while the density of the hydrogel can be tuned by the amount of OMP used. Since the negative charge of POMs, the MOMPs network was a potential superabsorbent materials, which can incorporate hydrophilic nano-objects. As a demonstration, magnetic particles, such as \( \gamma \)-Fe\(_2\)O\(_3\), was incorporated to the OMP-based hydrogel. Similarly, copolymerization of these OMPs with methyl methacrylate and ethylene glycol dimethacrylate yielded networked MOMPs, which can swell in organic solvent, such as CH\(_3\)CN, DMF, DMSO, and etc [62]. The presence of POMs in the network played an important role, as for the POM-free hydrogel the degree of swelling was much smaller than the corresponding MOMPs. These MOMPs displayed macroporous structure and can be used as catalyst for the sulfide oxidation under heterogeneous condition.

Using the UV initiated copolymerization of divinyl functionalized OMPs 57, 58 with \( \text{t-butyl} \) acrylate and hexanediol diacrylate, Herring groups prepared POMs-containing films with different amount of POM loadings [63,64]. They found that the water uptake was strongly related to the POMs in the resultant films, which facilitated the fast transportation of protons.

Instead of free radical polymerization, Yan and coworkers

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Fig. 16. (A) Preparation of PCL-POM-PCL MOMP 47 by using OMP 46 as initiator; (B) preparation of MOMP 50 by using OMP 49 as monomer; (C) preparation of OMP-containing polypeptide 52 from protected OMP 51; (D) post-modification to preparation MOMp 54 through click chemistry.

Fig. 17. Structures for di- and multi-vinyl modified OMPs.
developed a facile preparation of MOMP s through precipitation polymerization between hexachlorocyclotriphosphazene (HCCP) and functional group symmetrically modified POMs [65]. The functional group used in this case can be hydroxyl, amino, phenolic, and so on, and the POMs can be varied from \([\text{MnMo}_6\text{O}_{18}]^{3-}\), \([\text{XW}_{11}\text{O}_{39}]^{3-}\) \((X = \text{Si, P})\), \(\text{z}_{2}-[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}\), as well as \([\text{V}_6\text{O}_{13}]^{2-}\).

Given by the rigid structure of POMs, the porous structure can be maintained in the resulted MOMP s, while the pores used to collapse in the case of organic linker. Meanwhile, the native negative charges on POMs together with its porous structure enabled the charge selective interaction with different molecules, as demonstrated by the selective adsorption of positive charged organic dyes. This materials can be used as potential absorbent and catalyst for polluted water.

Hill group reported a \([\text{V}_6\text{O}_{13}]^{2-}\)-based MOMP through the esterification between \(\text{C}_3\)-symmetric trifunctioned 1,3,5-benzene-tricarboxamide and \([\text{H}_3\text{V}_6\text{O}_{13}]^{3-}\) cluster (Fig. 18A) [66]. The structure of the resulted MOMP was fully characterized by \(^{13}\text{C}\) NMR. It can form gel by adding organic solvent as well as organophosphorus (OP) agent analogues. Taking advantage of the catalytic oxidation property of \([\text{V}_6\text{O}_{13}]^{2-}\), OP can be degraded to nontoxic molecules.

Sonogashira–Hagihara cross-coupling can also be used in the construction of network MOMP. Chen and coworkers synthesized two tetrabromo-bifunctionalized Anderson-type POMs 59 and 60, which were then reacted with 1,3,5-triethylbenzene to form conjugated microporous polymers (Fig. 18B) [67]. The resulted MOMP exhibited porous structure with Brunauer–Emmett–Teller (BET) surface areas up to 200 m\(^2\)/g. Such kind of porous structure and well dispersed catalytic POM centers endowed the MOMP with high photocatalytic activity as demonstrated by the degradation of dye molecules under visible light.

The electrochemical polymerization to prepare MOMP s was developed by Hasenknopf and coworkers (Fig. 19). In principle, pyridine group can undergo a nucleophilic attachment to the meso positions of the porphyrin under electrochemical oxidation condition. Therefore, if the pyridine groups came from difunctionalized POMs, it can form polymeric network with zinc octaethylporphyrin (ZnOEP) bearing four nucleophilic attack positions. Using the esterification method, pyridine groups can be introduced different POMs including Anderson type \([\text{MnMo}_6\text{O}_{18}]^{3-}\) 61 [68], Linquist type \([\text{V}_6\text{O}_{13}]^{2-}\) 62 [69], as well as Dawson type \([\text{P}_2\text{W}_{15}\text{V}_5\text{O}_{62}]^{9-}\) 63 [70–72]. In such kind of MOMP s, the porphyrins acted as photosensitizer and allowed the activation of POMs under visible light instead of UV. Upon photo excitation of the porphyrin, the POM units were reduced and can be used in the preparation of Ag\(^{0}\) nanowires and triangular nanosheets [68].

Coordinative ligand modified POMP s can also act as hybrid ligand to form coordination frameworks by interaction with different metal ions. Hill group reported the formation of 3-D coordination network by reacting pyridine symmetrically modified \([\text{V}_6\text{O}_{13}]^{2-}\) cluster 62 with different divalent transition-metal ions [73]. Chemically, a coordination polymer chain was first formed, which was then connected to each other by hydrogen bond to form the final 3-D network. By changing the pyridine group to carboxyl acids, they also built a 3-D coordination network by reacting with \(\text{Tb}^{3+}\) [74]. The catalytic activity of \([\text{V}_6\text{O}_{13}]^{2-}\) cluster was greatly enhanced by 2 times in the aerobic oxidation of \(\text{PrSH}\), when comparing with the carboxyl acid modified \([\text{V}_6\text{O}_{13}]^{2-}\) itself.

Furthermore, making use of the coordination chemistry between pyridine and Cu\(^\circ\), Yang group achieved the construction of heterometallic cluster organic frameworks by choosing the pyridine modified \([\text{MnMo}_6\text{O}_{18}]^{3-}\) [75].

By modifying Anderson \([\text{MnMo}_6\text{O}_{18}]^{3-}\) cluster symmetrically with admantane, the resulted OMP 64 can form host-guest complex with polymerizable \(\beta\)-CD, which can be chemically crosslinked to form a hydrogel (Fig. 20) [76]. Interestingly, hydrogel cannot be prepared by treating the \(\beta\)-CD-containing polymer with OMP cluster symmetrically modified by admantane, which emphasizing the important role of the host-guest complex.

Post-modification of 3-D polymeric network, such as resin, can also be used to prepare MOMP network. Wang group modified the surface of macroporous resin with terminated alkylnyl groups, which was then clicked with azide difunctionalized Dawson type \(\text{P}_2\text{W}_{15}\) [77]. The OMPs covalently loaded macroporous resin can be used as heterogeneous catalyst in the oxidation of tetrahydrothiophene (THT). Due to its porous structure and covalent connection, the MOMP catalyst exhibited high selectivity and efficiency, as well as stability.

2.4. Discrete metallomacrocycles and their hierarchical structures

Besides coordination networked MOMP s, some interesting discrete metalloccycles were also reported by using coordinative ligand modified POMs as building blocks. Izzet, Proust and coworkers carried out pioneered work in this area. To make discrete metallomacrocycle instead of coordination polymer, how to control the angle between two ligands became very important. Therefore, in this case, the organosilyl derivatives of monovacant POMs were used, where the rigid coordinative ligand can be introduced through Sonogashira cross-coupling reaction.

By using the rigid and conjugated connection, the angle between two ligands can be tuned to either 60° or 90° depending on the solvent used. For example, as shown in Fig. 21, by using the pyridine difunctionalized Dawson type OMP 66 to interact with 180° metal acceptor units, such as trans-[\(\text{OC}_{2}\)] or trans-[\(\text{PtCl}_{2}\)], a triangle metalloccycle was obtained [78]. The formation of such kind of triangle structure was demonstrated by travelling wave ion mobility mass spectrometry (TWIM-MS), diffusion-ordered NMR spectroscopy (DOSY), as well as small angle X-ray scattering (SAXS).
Fig. 19. Preparation of network MOMPs by electrochemistry: (A) Anderson type [MnMo₆O₁₈]^{3+} 61 and Linqvist type [V₆O₁₃]^{2-} 62-containing MOMPs; (B) Dawson type \([P_2W_{15}V_{13}O_{62}]^{3+}\) 63-containing MOMP.

Fig. 20. Schematic illustration of the preparation of MOMP based on host-guest interaction using OMP 64. Reproduced from Ref. [76], with permission from Copyright (2017) Royal Society of Chemistry.
While for the less charged (3-) Keggin type OMP bearing the same coordinative groups as the previous more charged (6-) Dawson type OMP, a mixture of triangle and square were observed by interacting with trans-[PdCl₂(MeCN)₂]\textsuperscript{79}. The proposed formation process is as follows: by adding 0.5 equiv. of metal salt, the species formed in solution probably corresponded to dimer with uncoordinated ligands; after increasing to 1.0 equiv., the triangle and square formed with identical distribution, as indicated by the NMR integration. This result also implied the unique role of the charge of the POMs in their self-assembly processes that disfavors the formation of large assemblies.

Apparently, it is possible to tune the structure of the metallo-cycles by changing either the coordinative ligand or the metal ion used or their counterions. Terpyridine was chosen to graft on Dawson type OMP \textsuperscript{67}, whose structure was similar to the previous pyridine modified OMPs. By interacting with 1 equiv. of [Fe(H₂O)₆]ClO₄\textsuperscript{2-} in DMSO, triangle assemblies were observed. While in the solvent of DMSO/CH₃CN (1:4, v/v) mixture, the same reaction condition gave an aggregation of the triangles \textsuperscript{80}. It should be noted that once CH₃CN was removed from the mixed solvent, the triangles were restored again. SAXS experiments indicated that there were ca. 54 triangles in the aggregated structure, in which the triangles were glued by the intermolecular electrostatic interactions between POMs and positive charged Fe\textsuperscript{2+}.

In further study, they used the easily oxidized [Co(H₂O)₆]NO₃\textsuperscript{2-} as metal ion, which allowed the study the difference of metal ions as well as the potential to control the supramolecular organization by redox chemistry \textsuperscript{81}. Similar to the results of [Fe(H₂O)₆]ClO₄\textsuperscript{2-}, Co\textsuperscript{II} also formed discrete triangle and square in solution. After oxidizing to Co\textsuperscript{III} by tribromide, large aggregates were observed by SAXS. The solvent composition also exhibited different behaviors for Co\textsuperscript{II} and Co\textsuperscript{III} complexes. In the case of DMSO-MeCN mixture, addition of MeCN to the DMSO solution of Co\textsuperscript{II} led to the formation of nanoaggregates, which was similar to the case of Fe\textsuperscript{II}. While for Co\textsuperscript{III}, worm-like structures formed, which may resulted from the aggregation of different nanostructures. For the addition of water to the DMSO solution of either Co\textsuperscript{II} or Co\textsuperscript{III} complex solution, only worm-like structures were observed, indicating in the presence of excess amount of water only the worm-like nanostructures were stable regardless of the charge of the metal linker.

2.5. Dendron and dendrimer

A special MOMP is OMP-containing dendrimers or dendrons. Hill group reported the first example of POM-containing dendrimers by covalent grafting \textsuperscript{82}. As shown in Fig. 22, it can be prepared by reacting a four arm tris(hydroxymethyl) ligand with \textsuperscript{P₆W₁₅V₃O₆₂}\textsuperscript{9-}. The presence of \textsuperscript{P₆W₁₅V₃O₆₂}\textsuperscript{9-} endowed the resulted dendritic MOMP with catalytic activity. With \textsuperscript{r-BuOOH} or H₂O₂ as oxidant, such MOMP can catalyze the oxidation of thioether tetrahydrothiophene, which was even better than a strong Brønsted acid p-C₇H₇SO₃H. The MOMP-based catalyst can be easily recycled and can be reused without any loss in catalytic activity.

Alternatively, dendritic MOMP can be prepared through the postmodification of reactive group functionalized dendrimers, such as poly(amido)amine (PAMAM), which allowed to load more POMs. For example, mannose-functionalized PAMAM and hydroxyl-functionalized PAMAM dendrimers were used to react with \textsuperscript{P₆W₁₅V₃O₆₂}\textsuperscript{9-}, which can introduce as much as 30 POMs in one dendrimers \textsuperscript{83}. In another case, Neumann group reported polypropyleneimine dendrimers-based MOMP \textsuperscript{71} through the reaction of the reaction of a tin chloride-substituted POM \textsuperscript{70}, with the primary amines in the dendrimers \textsuperscript{84}.

Instead of dendrimers, nanoparticles, such as nanolatex, can also be used as platform to prepare dendritic MOMP. Mayer group reported such kind of materials by a facile reaction between mercaptopropyl-functionalized POM and benzyl chloride on the nanolatex \textsuperscript{85}. Polymerizable groups modified OMP can also be used as surfactants in the emulsion polymerization of other monomers \textsuperscript{86}. After the copolymerization, POMs could be covalently grafted to the surface of the polymer latex. With the catalytic POMs on its surface, this kind of MOPMs may be used as quasi-homogeneous catalysts.

Taking advantage of the incompatibility between charged POM

Fig. 21. Synthetic procedure for coordination side modified OMPs 66 and 67, and the typical metallo-triangle and metallo-square formed by OMP 67.
and neutral polyhedral oligomeric silsesquioxane (POSS), Wang group achieved the construction of mesoscale graphene-like honeycomb mono- and multilayers by covalently bond of these two building blocks, as shown in the high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) (Fig. 23) [87]. They designed a dendron-like conjugate with four POSS on one end and one \([\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]^{9-}\) cluster on the other end. It revealed a hierarchical process and the key role of intermediate states in determining the honeycomb structure. In a most recent research, they also found that such kind of Janus dumbbell can form cubosomes phase [88].

3. Conclusions and outlook

One of the key research focus of metallopolymers is the development of new metal-containing building blocks. There are several basic characteristics for a good metal-containing building block regarding to applications: (i) it should be easily prepared and can be scale up; (ii) many different metal elements can be incorporated; (iii) it should be very stable both chemically and physically; (iv) it should be polymerized very easily through different polymerization technologies. This review focuses on a special metal-containing building block, named organically modified polyoxometalates.

As a very important class of compounds in inorganic chemistry, POMs have been studied and applied in both academic and industry. Initially, to avoid their disadvantages, such as poor solubility in organic solvents, poor compatibility with organic molecules and substrates, and so on, organically modification of POMs was developed. Starting in early 1990s, incorporation of POMs into polymers became a new option, although it was not that efficient in the very beginning. With the development of organically modified POMs and promoted by the progress in polymer chemistry, POMs-containing polymers have gained momentum. Due to the multiple elements in POMs, MOMPs have already been used as “green catalyst”, chemical sensor, photochromic materials, high density...
data storage materials, diectric materials, and so on. Although lots of MOMPs were prepared and many potential applications were demonstrated, there are still several major obstructions which limit the development of such kind of materials. Firstly, limited variation of POMs and modification chemistry have slowed down the development of new MOMPs. As we mentioned, there is plenty of room for the development of MOMPs and the discovery of new functions. Secondly, the difficulty in synthesis and purification of MOMPs also obstruct the development of MOMPs and their practical applications. As a highly negative charged cluster, OMPs cannot be purified by classical organic methods, such as chromatography. Successful preparation of OMPs much relies on high efficiency organic chemistry. Therefore, high efficiency chemistry and purification methods, as well as polymerization techniques will be urgent in this area. Thirdly, how to achieve practical applications for MOMPs? As reported, POMs are very promising candidate in many area, including high efficiency catalysis [18], anti-HIV drugs [30], and so on. To avoid the leakage of catalyst in industrial application as well as their cytotoxicity in biomedical application, incorporation of POMs into polymers is one of the best strategies. To achieve practical application, practical preparation of such materials is still challenging, which relies on the development of synthetic chemistry and purification techniques.

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Appendix A. Supplementary data

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References