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Covalently-linked polyoxometalate-polymer hybrids: optimizing synthesis, appealing structures and prospective applications

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Polyoxometalates (POMs) are a class of polyanions that have fixed metal-oxygen frameworks composed of early transition metals in high oxidation states (most commonly V^V, Mo^{VI} and W^{VI}). The diversity in composition and configuration endows POMs with fascinating chemical and physical properties, as well as prospective applications in photochromic or electrochromic materials, catalysts, nano-structural materials, medicines and so on. In order to develop more advanced materials based on POMs, a lot of effort has been paid on exploiting new types of POMs and combining POMs with other functional units through non-covalent modifications or covalent bondings. Among these delicate works, integrating inorganic POMs with organic polymers into diverse hybrids through covalent linking is a quite interesting field. We present here a perspective review on the synthesis of POM-polymer hybrids (PPHs) based on covalent modifications, their hierarchical structures and potential applications.

Introduction

Polyoxometalates (POMs), a class of polyanionic clusters, possess intriguing properties in catalysis, novel materials and chemical biology.[1,2] Aiming at improving and creating more functionalities based on these intriguing clusters, many researchers have done masses of innovative works on organic modification of POMs.[3,4] In general, modification methods of POMs can be divided into two main categories, *i.e.* non-covalent (electrostatic, hydrogen bond or van der Waals interaction) modification and covalent modification.[5] For the former type, numerous achievements have been accomplished through crystal engineering and supramolecular cooperations.[6,7] Covalent modification of POMs, by contrast, started much later and has limited successful outcomes. In recent years, embedding inorganic POMs into organic or inorganic matrices has received significant attentions as a robust way to fabricating novel composite materials.[8,9] The fabrication methods of composite materials also can be roughly sorted into non-covalent and covalent types. Simply blending or dispersing functional POM components in silica resins, zeolites or polymer resins is relatively convenient compared to covalent embedding and the resulting performance is adequate for basic applications of POM like

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catalysis.[10-12] However, there are some inevitable drawbacks of these non-covalently fabricating materials like the leakage of POM components and the imprecise anchoring sites which profoundly influence the sophisticated applications of POMs as nanomaterials.

On the other hand, in covalently-linked POM-polymer hybrids (PPHs), POMs are firmly fastened on the polymer matrix and anchoring sites can be precisely programmed through reasonable molecular design.[13,14] These characteristics determine the distinctive features of covalent PPHs different from those non-covalent blends. Several strategies have been developed to synthesize PPHs including direct polymerization like free radical polymerization, atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT), ring opening metathesis polymerization (ROMP) or post-polymerization grafting methods. With multiple synthetic routes, various PPHs containing different POM clusters with diverse structures have been obtained and can be roughly sorted into four categories according to their chain configurations. The first kind is crosslinked PPH, in which bifunctional or multifunctional POMs are tethered to organic networks through covalent bonds. Crosslinked PPHs are mainly obtained by free radical copolymerization of organic monomers and POM based crosslinkers. The second kind is side-chain PPHs, in which POMs are placed at the side-chains. This type of PPHs are obtained primarily through the polymerization of POM based monomers with only one polymerizable unit other than those POM based crosslinkers. The third kind is backbone PPH, with POMs embedded in the polymer backbones. This type of PPHs are generally synthesized by condensation polymerization methods or stepwise click reactions. And the last kind is relatively simple from the sight of molecular structure and synthetic strategy, which is composed of a POM head and one or more polymer tails. Hence we nominate the fourth kind hybrid as head-tail PPH (Fig. 1).

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Wei Wang obtained his Ph.D. degree in Polymer Physics Chemistry under the supervision of Prof. Welheim Ruland at Philipps-University of Marburg in 1993. Then he moved to Kyoto University to take up a postdoctoral research on the fundamental physics of liquid crystalline polymers with Prof. Takeji Hashimoto. After worked as a research fellow in Toray Industries (Japan) and Institute of Materials Research and Engineering (Singapore), he started his independent academic career in 2002 when he joined Nankai University as a distinguished professor. He puts his research emphasis on the fabrication of novel hybrid materials through bottom-up constructing strategy.

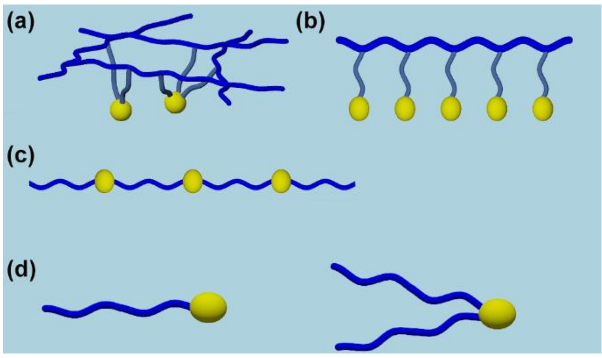

Fig. 1 Four categories of covalent PPHs according to their chain configurations: (a) crosslinked PPHs, (b) side-chain PPHs, (c) backbone PPHs and (d) head-tail PPHs. The yellow ellipsoids and the blue chains represent the POM clusters and organic polymers respectively.

As a unique class of nano-building blocks, POMs always possess strong oxidizing property, intensive charge effect and concrete structures. Although these intrinsic characters endow POMs with distinctive and outstanding properties in fabricating novel functional materials, they set up series of obstacles in synthesis and characterization of PPHs on the other hand.[15-20] Especially due to the nucleophilic character of the oxygen atoms on the surface, the intrinsic anionic nature and the relative large size of POMs, it is hard to modify POMs with required functionalities without disturbing the interesting features of inorganic POMs. Hence it is quite challengeable to choose proper polymerization or hybridization methods to fabricate covalent-type PPHs compared to those non-covalent blending POM/polymer composites. But considering the inherent drawbacks of non-covalent modification like inevitable leakage of toxic elements or undesired macroscopic phase separations,[21-23] the painstaking exploration of PPHs with firm connection between inorganic components and organic matrices appears its significant importance. The intensive contrast in electron density between POM and organic composition together with the robustly fixed shapes of POM clusters greatly benefit the study of the fundamentals of self-assembling process as we can observe the microscopic structures directly by transmission electron microscope without any detrimental staining.[24-27] Moreover, the flexible adjustability in chain structures, organic components and peripheral counterions endow PPHs with nearly infinite possibility in constructing novel organic-inorganic hybrid composites. Other than the attractive self-assembled structures, the potential applications of PPHs in proton conducting membranes, heterogeneous catalysis and nanofabrication have also received lots of attentions. Here, we will briefly review the evolution of synthetic methods, intriguing self-assemblies and prospective applications of four types of PPHs based on covalent modifications.

Crosslinked PPHs

Just as their name implies, crosslinked PPHs are mainly composed by copolymerizing organic monomers with POM based crosslinkers through free radical polymerization method.

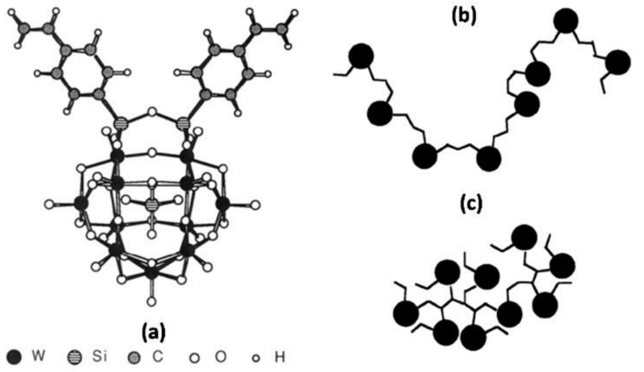

Fig. 2 (a) Structure of the $[SiW_{11}Si\text{-styryl}]^{4-}$ monomer; proposed structures for $SiW_{11}SiR$ polymers (b) linear and (c) branched.[28] Reprinted with permission from Ref. 28. Copyright (1992) American Chemical Society.

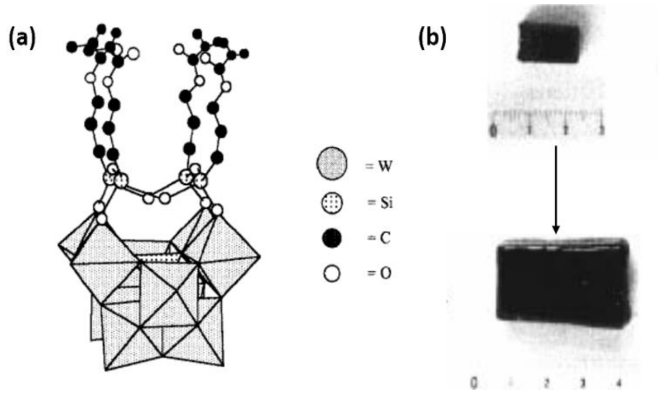

Fig. 3 (a) Polyhedral representation of POM crosslinker $[\gamma\text{-}SiW_{10}O_{36}(RSiO)_4]^{4-}$ (R = $C_3H_6OC(O)C(CH_3)=CH_2$); (b) swelling test of a hybrid POM gel loading magnetic particles.[30] Adapted from Ref. 30 with permission from John Wiley and Sons.

The first report of crosslinked PPHs is in 1992, Judeinstein demonstrated the polymerization of four types of POM based monomers into $SiW_{11}SiR$ kind polymers based on lacunary $[SiW_{11}O_{39}]^{4-}$, which is also the first reported covalently bonding PPHs.[28,29] He then examined the effect of polymerization conditions (like solvent, catalyst and temperature) on all four monomers and found out the styryl-derived monomer displaying relatively higher polymerization activity in polar solvents like propylene carbonate and DMSO. After confirming the structure integrity and the preservation of electrochemical property of POM clusters by NMR, IR and cyclic voltammetry (CV) spectra, he claimed successful syntheses of the first PPHs. According to the results of quasi elastic light scattering (QELS) measurements, he proposed two structure models to the hybrid polymers (Fig. 2). Although the linear structure (Fig. 2b) seems reasonable to some degree if we take the intensive steric effect of POM clusters into consideration, we still believe that branched structure is more realistic for those poorly controlled and randomly crosslinked PPHs considering the essence of radical polymerization.

Following the pioneering work done by Judeinstein, Mayer, Thouvenot and their coworkers developed several crosslinking agents based on a divacant polyanion $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ unit (see one example in Fig. 3a).[30,31] After then, they copolymerized these polymerizable POMs with other organic monomers like acrylamide or ethyl methacrylate into hybrid covalent networks with POM clusters hanging on them. Such copolymers can form organogels or hydrogels on account of different peripheral counterions around the POM clusters. More interestingly, they also reported the incorporation of magnetic nanoparticles ($\gamma\text{-}Fe_2O_3$) into the hybrid networks based on POMs and polyacrylamide as showed in Fig. 3b. The entrapped nanoparticles maintained the rotational mobility in the hybrid network and displayed a size-determined fractional release during the swelling process. The detailed study on the effect of the ratio of POM based crosslinkers was also described clearly. Moreover, through introducing an ammonium salt ($[(Me)_3N^+C_2H_4OC(O)C(CH_3)=CH_2]$) bearing a polymerizable methacrylate group, the crosslinking ability can be further improved and resulted in the decrease of gel solvation.[32]

Recently, analogous works have been done by Herring and coworkers on investigating proton-conductive membranes based on copolymerization of POM derived crosslinkers. Through copolymerizing divinylsilyl-11-silicotungstic acid ($H_5[SiW_{11}O_{40}\{Si(CH=CH_2)\}_2]$) with butyl acrylate and 1,6-hexanediol diacrylate, they obtained novel proton-exchange membranes with various POM loading amounts for fuel-cell applications. The immobilization of the proton conducting components, which are POM clusters with H^+ as counterions, in the membrane through robust covalent bonds can avoid the leakage of functional water-soluble components. Fast proton transport in these hybrid materials was facilitated by as few as three water molecules per proton. Some of these hybrid photon-conductive membranes even demonstrated higher proton conductivities than the commercially produced perfluorosulfonic acid (PFSA) polymers.[33,34]

Carraro, Bonchio and their coworkers also utilized multifunctional POMs as crosslinkers in fabricating various sustainable oxidation catalyses. They designed and synthesized three different POM crosslinkers with two or four polymerizable octenyl tails covalently attached on each as showed in Fig. 4a. They further copolymerized these three POM monomers respectively with methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EDM) in mixed solvent with 1,4-butanediol/2-propanol=1/2 as porogenic agent. After confirmed successful polymerization of crosslinked PPHs and intact POM structures by Fourier transform infrared spectroscopy (FT-IR), they estimated by thermogravimetric analysis (TGA) that about 65% of multifunctional POM had been cross-linked within the final polymeric materials which displaying a catalytically favoured porous architecture (Fig. 4b). These immobilized heterogeneous catalysts can activate hydrogen peroxide in various solvent environments. The firm anchoring of catalytically activated POM ensured the good recyclability of these heterogeneous catalysts. As demonstrated by their recycling experiment, the hydrogen peroxide conversion can reach satisfactory levels with recovered catalysts and the FT-IR spectra did not show obvious differences. Especially, these hybrid polymeric materials can catalyse two-step oxidation of dibenzothiophene, which demonstrated their potential in fuel oxydesulfurization.[35]

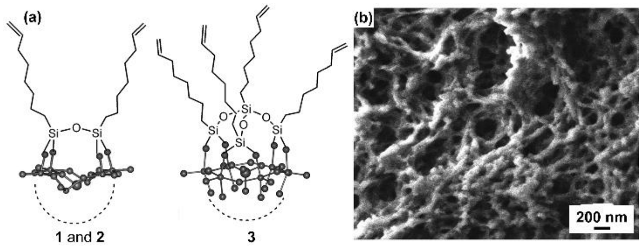

Fig. 4 (a) Molecular structures of three octenyl-derived POM crosslinkers TBA_3H [$\{CH_2=CH(CH_2)_6Si\}_2O(\alpha\text{-}SiW_{11}O_{39})$] (**1**), TBA_3H [$\{CH_2=CH(CH_2)_6Si\}_2O(\gamma\text{-}SiW_{10}O_{36})$] (**2**), and TBA_3H [$\{CH_2=CH(CH_2)_6Si\}_4O_3(\alpha\text{-}SiW_9O_{34})$] (**3**), TBA is the abbreviation for counterion tetrabutyl ammonium; (b) SEM image of hybrid polymer synthesized by copolymerizing POM crosslinker (**2**), MMA, EDM.[35] Reproduced from Ref. 35 with permission from John Wiley and Sons.

Inspired by the work done by Carraro *et al.*, we proposed another convenient way to immobilize catalytically active POMs by utilizing classical click chemistry. D380 macroporous benzylamine resin was selected as the polymeric matrix and modified by pent-4-ynoic acid. A monovacant polytungstate was chosen as active inorganic component and reasonably derived to be equipped with two azide groups (the formula is $(TBA)_6[\alpha_2\text{-}P_2W_{17}O_{61}(SiC_6H_4CH_2N_3)_2O]$). The click reaction was conducted in DMF solution at 45 °C for 48 h. The intact framework of POM and efficient covalent bonding can be confirmed by FT-IR characterization. The X-ray photoelectron spectroscopy (XPS) result also validated the tungsten of POMs is in its fully oxidized state. Furthermore, the catalytic efficiency and selectivity of this POM-decorated macroporous resin was evaluated in the oxidation of tetrahydrothiophene (THT), a well-known gasoline contaminant. Other than high efficiency and selectivity, this POM-decorated macroporous resin can be recycled and reused continuously for many times without any detectable loss of catalytic activity and leakage of inorganic components.[36]

Zhang and coworkers modified the heteropolymolybdate with methacrylic anhydride through the amino group thereby successfully synthesized an Anderson-type POM with two alkenyl groups. They further copolymerized it with methyl methacrylate (MMA) with 1,1'-azobis(cyclohexanecarbonitrile) (ABCN) as initiator in acetonitrile. Considered the intrinsic multilevel redox character of Anderson POM, the resulted backbone PPH was carefully studied on its potential as a ternary resistance switching memory. The multilevel memory devices fabricated by such PPH exhibited rewriteable switching properties, good endurance with distinct operation windows and long retention.[37]

Yin, Liu and coworkers designed and synthesized a hybrid amphiphile with chemical formula as $K_3PW_9O_{37}(SiC_7H_{11}O_2)_4$. This hybrid amphiphile was easily obtained by modifying trivacant Keggin clusters with silane-coupling agent under acidic conditions. They utilized this polymerizable hybrid as stabilizing surfactant and crosslinking agent in the emulsion polymerization of styrene. The obtained hybrid latex exhibits a typical core–shell structure with a PS core and a POM shell. This POM decorated latex can be used as heterogeneous catalysts, which can be conveniently recycled through centrifugation or other simple operations.[38]

In conclusion, synthesizing crosslinked PPHs is the earliest example of the fabrication of covalent PPHs. The synthetic method to obtain crosslinked PPHs so far is still confined to the free radical polymerization. With this approach, it is very difficult to control the loading amount and the anchoring site of functional POMs. Nevertheless, crosslinked PPHs initiated a new area in constructing hybrid organic-inorganic nanocomposites. The hybrid networks of crosslinked PPHs are suitable for catalytic applications. With robust linking between POM clusters and organic networks, the crosslinked PPHs can be recycled without obvious decrease in catalytic activity and detrimental loss of inorganic components. As the realization of crosslinked PPHs or other covalent PPHs is closely related to the development of covalent modification methods of POMs, we can definitely anticipate the incorporation of more complicated and powerful POM clusters into the crosslinked PPHs. Composing hierarchical nanocomposites through embedding other functional components like metal nanoparticles, bioactive molecules *etc.* into the PPH networks will be interesting too. More fundamentally, finding ways to control the loading amount and the overall distribution of POM clusters also deserves our attention.

Side-chain PPHs

Side-chain PPHs are composed of pure organic backbones and inorganic POM pendants. Compared to crosslinked PPHs, side-chain PPHs are more regular in structure. The first side-chain PPH was reported by Maatta and coworkers. They took an imido derived way to organically modify Lindqvist hexamolybdate. Through reacting $TBA_2[Mo_6O_{19}]$ with $Ph_3P=NC_6H_4C=NCH_2$ in pyridine solution at 90 °C, the styrylimido-hexamolybdate hybrid can be obtained in satisfactory yield. Similar to the cornerstone work done by Judeinstein, this styryl modified organic-inorganic hybrid can readily undergo conventional free radical induced copolymerization with 4-methylstyrene in 1,2-dichloroethane and using azobisisobutyronitrile (AIBN) as initiator. They hence claimed the successful synthesis of POM grafted PPH merely with IR and NMR characterization of the final PPH. Based on the NMR signal intensity, they suggested that the ratio of hybrid monomer to organic monomer was about 1/3.[39]

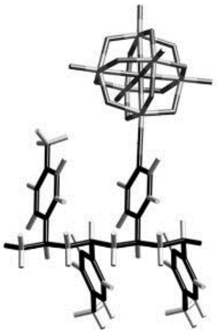

Fig. 5 Idealized representation of a segment within the side-chain PPH synthesized by Moore *et al.*[39] Reproduced from Ref. 38 with permission of The Royal Society of Chemistry.

However, there is no further results reported on this side-chain PPH, even they declared that further characterization and studies on a variety of other polymerizable organoimido systems were underway at the end of the paper. Therefore we have sufficient reason to believe that such copolymerization is not very controllable and may result in some more complex branched polymers rather than simple linear polymer.

Peng's group also make critical contributions in designing and realizing side-chain PPHs based on conjugated organic backbones through imido modification of Lindqvist hexamolybdates. Peng and his coworkers made their first attempt on synthesizing four side-chain PPHs with POMs tethering to a poly(phenylene ethynylene) (PPE) backbone as pendants through rigid conjugated or flexible alkyl bridges respectively. The difference in covalent attachment led to the variance in optical properties, that conjugated tethering polymers had a higher fluorescent quenching effect than those with flexible alkyl bridges, which indicates a dominant through-bond photoinduced electron transfer mechanism. Aside from condensation polymerization process, one-pot hybridization/polymerization was also confirmed to be feasible in constructing such photoactive side-chain hybrid polymers. Other than traditional NMR determination on the successful synthesis, gel permeation chromatography (GPC) measurement, to the best of our knowledge, was applied in the detection of molecular weights of PPHs at the first time. Due to the quite rigid backbone structure of PPE and bulky substituent POMs, the average molecular weights presented by GPC method based on PS calibration obviously deviated from the real values. Hence they also conducted light-scattering experiments to determine the real molecular weight of such side-chain PPHs and gave a confident data. With the average molecular weight and elemental analysis result, they can roughly estimate the grafting degree as four to five POMs on each polymer chain.[40,41]

Although above-mentioned side-chain PPHs had demonstrated certain potential in photovoltaic materials with POM clusters as electron acceptors and organic π-conjugated segments as electron donors, their photovoltaic performances turned out to be not very attractive. As high efficient photovoltaic materials require not only effective photo-induced charge transfer but also sufficient and separate charge transporting pathways for charge carriers, appropriate microphase separation is often favoured in fabricating superior photovoltaic devices. Thereafter, Peng and coworkers dedicated vast efforts to synthesize diblock photoactive copolymers of side-chain PPHs in order to further improve the power conversion efficiency of conjugated PPHs. The first reported POM-containing diblock copolymers were obtained by post-polymerization hybridization through grafting inorganic POM clusters to poly(2,6-dimethyl-4-vinyl aniline)-poly(phenylene vinylene), which is a block copolymer precursor with amino reactive sides settled in the polystyryl-like flexible block. Such block copolymers with POMs as functional pendants displayed two absorption bands owing to the ligand-to-metal charge transfer transition of imido-functionalized POM clusters and the π-π* transition of poly(phenylene vinylene) backbone respectively. However, the attachment of POM clusters had not brought effective phase separation into the films cast from those side-chain block copolymer type PPHs. They further translated the rigid block, *i.e.* the poly(phenylene-vinylene) block, into a poly(3-hexylthiophene) block, which shows more intensive tendency in microphase separation with polystyryl-type blocks. Although the spin-cast films of such improved polymers displayed worm-like conducting domains with general width lower than 50nm, their power conversion efficiencies are still believed to be not very high.[42-44]

Concluded from above-mentioned results, both post-polymerization hybridization and one-pot hybridization/polymerization are currently incapable to well control the grafting numbers and positions of POM components on the side-chain PPHs. To address this problem, we introduced ring opening metathesis polymerization (ROMP) into the preparation of side-chain PPHs, which is a living and controllable polymerization method. Since then, we have propelled the synthesis of side-chain PPHs to a precisely regulated stage that never reached by traditional polymerization or hybridization means. In detail, we first synthesized a POM based hybrid monomer with a norbornene-type polymerizable unit through a simple three-step organic reaction. In order to create a robust connection between the inorganic component and the organic backbone, we applied the highly-efficient esterification modification of V_3-capped Wells-Dawson-type POM ($[P_2W_{15}V_3O_{62}]^{9-}$, abbreviated as V_3POM). By modification with tris(hydroxylmethyl)-type derivative of norbornene, the obtained hybrid monomer can readily undergo polymerization (as illustrated in Fig. 6a) under the activation of Grubbs catalyst (ruthenium N-heterocyclic carbine). This polymerization process yielded well-defined linear side-chain PPHs with relatively high molecular weights and low polydispersities as demonstrated by the size-exclusion chromatography (SEC) results (as showed in Fig. 6b).

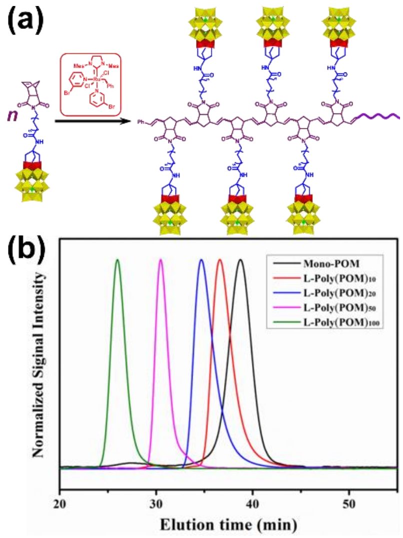

Fig. 6 The ROMP process of V_3POM-based monomers. (a) The illustration of ROMP process and (b) the SEC results demonstrated the well controlling of ROMP method.[45] Adapted with permission from Ref. 45. Copyright (2014) American Chemical Society.

Such linear polymers with V_3POM pendants can be cast into thin films from their acetonitrile solutions. The catalytic abilities of these side-chain PPHs were also carefully evaluated in the oxidation of THT and demonstrated high catalytic efficiencies as well as excellent durability in recycling.[45] As a controllable living polymerization method, ROMP is also feasible in synthesizing well-defined block copolymers with inorganic POMs covalently located in independent segments. Such works and further study on functional applications are smoothly ongoing in our group.[46]

Pradeep, Gonsalves and coworkers also had tentative tries on fabricating functional PPHs and focused on their potentials for nanolithography. They designed and synthesized a hybrid monomer by modifying V_3POM with trihydroxymethyl-derived methacrylamide. They further tried to copolymerize the hybrid monomer (the chemical formula is $[P_2V_3W_{15}O_{59}\{(OCH_2)_3CNHCO(CH_3)C{=}CH_2\}]^{6-}$) with photoactive monomers like (methacryloyloxy)phenyldimethylsulfonium triflate (MAPDST) or methylmethacrylate (MMA). Although they claimed successful synthesis of such polymer/POM hybrids with covalent linking, the characterization results were not adequate to verify their statement. Moreover, they attributed the TGA residual mass to the presence of about 0.3 or 0.5 POM cluster per polymer chain respectively, which further revealed a poor control on the polymerization process.[47] They also modified a Mn-Anderson POM in a similar way to give a bifunctional hybrid monomer with chemical formula as $(TBA)_3[MnMo_6O_{18}\{(OCH_2)_3\ (CNH)\}_2(CO(CH_3)C]CH_2)_2]$. Through copolymerizing this hybrid monomer with organic monomer MAPDST using free radical polymerization, they claimed that a new radiation sensitive polyoxometalate/polymer hybrid was obtained. However, their GPC characterization was very disappointing and the TGA result still indicated that not every polymer chain was attached with POM.[48]

In conclusion, side-chain PPHs are more regular in the molecular structure compared to crosslinked PPHs. Especially, the introduction of ROMP method dramatically promoted the synthetic strategy of covalent PPHs. The side-chain PPHs obtained by ROMP can possess high degree of polymerization together with narrow molecular weight distribution as confirmed by SEC equipped with a light-scattering detector. While we designed the hybrid monomer for the realization of ROMP in synthesizing PPHs, a long flexible linker was selected to reduce the steric influence of bulk POM clusters. It will be interesting to further investigate the effect of organic linker between the polymerizable unit and the POM cluster on the polymerization process. In addition, ROMP can be applied in fabricating block copolymers of PPHs too. With delicate molecular design and precise control in polymerization process, advanced performance or novel properties may be aroused in more complicated side-chain PPHs. Moreover, copolymerizing POMs with other functional inorganic building blocks like polyhedral oligomeric silsesquioxanes (POSS), fullerenes (C60) into block copolymers or multiblock copolymers will be very meaningful. The synergetic effect of various blocks with diverse functionalities in catalysis, photonics, bioactivity and so on may result in some unexpected innovations.

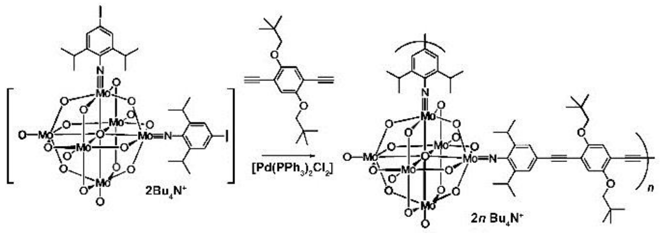

Fig. 7 Synthesis of POM-containing conjugated polymer through sonogashira coupling.[52] Reproduced from Ref. 52 with permission from John Wiley and Sons.

Backbone PPHs

Stepwise polymerization is mainly adopted in the construction of backbone PPHs, which fundamentally determines the uncontrollable nature of such category of hybrid polymers. On the other hand, the unique physical and chemical properties of inorganic POM clusters significantly influence the activity of functional group modified on POMs and further affect the post-functionalization process. Moreover, the steric hindrance of POM clusters seriously impedes the chain propagation of backbone PPHs. Hereafter, only a few results have been reported on the synthesis and functional study of backbone PPHs.

Incorporation of POM clusters into conductive polymers with the purpose of creating functional composites for energy conversation, energy storage or multi-responsive sensors by utilizing the multi-redox ability of POMs and charge transfer effects have received extensive attentions.[49] Aside from the utilization of the nucleophilicity of lacunary anions, Peng and coworkers developed a relatively precise derivation method based on Mo-N-C imido bond.[50,51] This particular method allows selective synthesis of bifunctionalized hexamolymbdate products by using the tetrabutylammonium (TBA^+) salt of the α-octamolybdate ion, $[\alpha\text{-}Mo_8O_{26}]^{4-}$ as starting material. By deriving aforementioned POM with 4-iodo-2,6-bis(1-methylethyl)benzenamine, a polymerizable monomer with two iodo functional groups can be readily obtained with over 60% yield. Through condensing this bifunctional monomer with 2,5-di(2,2-dimethylpropoxy-1,4-diethynylbenzene) under the catalysis of palladium, a backbone type PPH can be obtained (Fig. 7).[52] Such poly(phenylene ethynylene) (PPE) supported PPH can be used to fabricate simple single-layer solar cells with efficiencies up to 0.15%, which may be not very impressive. But their experiment still exploited a new way to engage POMs into photovoltaic materials. Considered that PPE only has limited absorption in the visible range and relatively poor charge-transporting properties, Peng and his coworkers further developed a more efficient backbone type conjugated PPH based on polythiophene. This polythiophene bridged PPH showed absorptions in the 400–550 nm range in dilute solutions and extended beyond 700 nm in thin films. Simple single-layer photovoltaic cell fabricated by this polythiophene based PPH harvested a power conversion efficiency of 0.24%.[53] In addition, this bifunctionalized monomer can copolymerize with other diiodo monomers to give fascinating copolymers.[54]

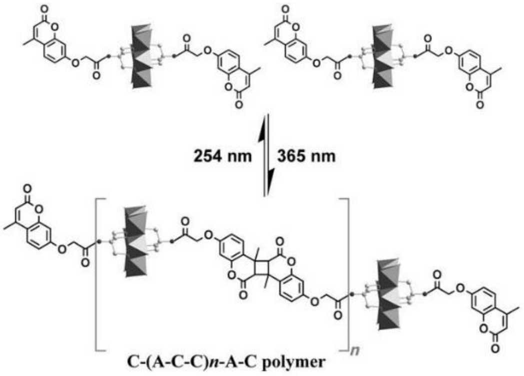

Fig. 8 Schematic representation of the reversible photopolymerization process of coumarin derived Mn-type Anderson POM.[57] Adapted from Ref. 57 with permission from John Wiley and Sons.

Moreover, Peng and coworkers also demonstrated a coordinated POM-containing hybrid polymer based on organoimido derivative POM, in which POM cluster and transition-metal complex are linked through an extended π-conjugated bridge.[55]

Another condensation polymerization to achieve POM-polyimide copolymer was carried out by Yang, Lu and coworkers using diamine modified divacant lacunary decatungstosilicate with chemical formula as $TBA_3H[\gamma\text{–}SiW_{10}O_{36}(NH_2CH_2CH_2CH_2Si)_2O]$. With robust imide bonds, the inorganic component can be firmly integrated into the organic backbone, which significantly improves the thermal and mechanical properties of the resulted polymer films. Moreover, the covalent embedding of POM clusters not only reserved the transparency of the polymer films, but also opened up a new approach to develop ultra-low dielectric constant (κ) hybrids or other functional materials. In their experiment results, the κ value can be as low as 1.22 with 10 wt% load content of inorganic POM clusters.[56]

Anderson-type heteropolymolybdate is another widely studied POM cluster, its symmetrical structure as well as convenient organic modification endows it with excellent ability in self-assembling process. In particular, the tris-(hydroxymethyl)aminomethane (TRIS) derivative of Anderson POM is often used as a multifunctional platform for covalent post-functionalization. With two active amino groups on each side, such organic-inorganic hybrid can be served as a versatile building block to construct novel functional materials.

Song and coworkers have done an interesting work based on TRIS derivative modified Mn-Anderson cluster.[57] They designed and synthesized a photosensitive organic-inorganic hybrid with two coumarin moieties on both sides. After thorough determination of this hybrid compound, they carried out a reversible polymerization by utilizing the characteristic ability of coumarin that it can form photoinduced cyclobutane dimers. By exposing the acetonitrile solution of coumarin derived Anderson POM to UV irradiation at 365nm, obvious colour change was observed that from light-yellow to deep-brown. Such colour change revealed a photoinduced polymerization of coumarin modified POM, which led to a C-(A-C-C)$_n$-A-C type backbone PPH with an average molecular weight (Mw) of 337.38 kDa and a polydispersity value of 1.60. Moreover, upon irradiation with shorter wavelengths like 254 nm, the photoinduced cyclobutane linkage can be broken. Therefore, the photoinduced polymerization process of coumarin modified hybrid monomer is reversible (Fig. 8).

Classical Cu-catalysed alkyne−azide cycloaddition (CuAAC click chemistry) was also applied in the synthesis of backbone oligomers embedded with Mn-Anderson type POMs. The strategy proposed by Cronin and coworkers is strictly step-by-step. In order to achieve a higher degree of polymerization, thorough functionalization of lower-grade oligomers is prerequisite. They reported four monodisperse oligomeric Mn-Anderson hybrids, from a dimer to a pentamer. Theoretically, polymers with higher molecular weight can also be obtained with monodispersion, but actually the decreasing in solubility of hybrid monomers and activity of end groups will definitely increase the synthetic difficulty.[58]

Overall, from the pioneering work done by Peng to the recently developed photoinduced polymerization of Anderson-type monomer, limited ways to achieve backbone PPHs have been exploited. Only stepwise polymerization has been proved valid in synthesizing various backbone POM-based hybrid materials. However, due to the steric effect and the electronic effect of POMs, it is not quite easy to obtain linear PPHs with narrow dispersion in molecular weight. Besides, as a class of rigid clusters, POM-implanting backbone PPHs have an intrinsic poor solubility even in strong polar solvents. This directly leads to a hindrance in precise determination of molecular weight. The solubility problem may be addressed by wrapping POMs with longer and more flexible organic cations. The uncertainty in polymerization degree and the wide polydispersity severely restrict the further development of backbone PPHs in applications as polymer materials. Hence, it is of fundamental importance to find a more controllable way to synthesize backbone PPHs.

Head-tail PPHs

As implied by a lot of experiment results, their unique physical and chemical properties tremendously influence the organic modification and self-assembly process of POM clusters. The fact that POM is quite different from both small molecules and polymers lead to an invalidation of empirical and theoretical principles that guiding the compositional or constructing operation of ordinary building blocks. And the uncertainty of chain structure, grafting number and modification position are often encountered in cases of other three type PPHs due to the poor control of polymerization or hybridization, which further complicates the POM-engaged processes. Therefore, some genuine propaedeutics should be understood first if we want to reveal the underlying facts of more complex POM based systems. Taking into consideration of well-defined structure and composition, the head-tail PPHs turn out to be ideal research objects for such purpose.

As the name implies, head-tail PPHs are composed of a rigid POM head and one or more flexible polymer tails that combined by covalent bonds. To the best of our knowledge, we proposed and successfully synthesized the first head-tail PPH with a V_3POM head and a polystyrene tail.[59] In addition, we first introduced atom transfer radical polymerization (ATRP) into the synthesis of PPHs. The V_3POM was modified by a trishydroxyl-derived bromoisobutyramide into a macroinitiator, which can initiate the ATRP of polystyrene into a head-tail PPH with definite one terminal POM on each polymer chain. With a well-defined structure, this head-tail PPH can be an ideal model for the study of POM participating self-assembly process. By simply replacing the peripheral TBA^+ cations around POM with protons through ion exchange, V_3POM-PS hybrid can assemble into vesicles in DMF solution. Moreover, the self-assembly behaviour of this head-tail PPH can be tuned by carefully controlling the annealing process. Upon adding H^+-resin, the POM head gradually turned hydrophilic but insoluble in DMF and the resulted giant amphiphile immediately assembled into imperfect vesicles with some small reverse micelles trapped in them. Such assemblies were considered in a metastable state so subsequent thermal annealing conducted to drive them toward thermodynamic stable state. After annealing at 70 °C, the size of vesicles obviously increased and the reverse micelles were eliminated as the tiny dark spots on TEM image disappeared. The enlarged flawless assemblies displayed a common appearance of conventional vesicles, however the thickness was larger than the value estimated by the equation of Azzam and Eisenberg. This phenomenon was caused by the rigid and incompressible essence of POM cluster, which forced the PS chain to take a more outstretched configuration.[60] Continuing the annealing process of large vesicles at ambient temperature further led to more intriguing morphological evolution, where the large vesicles were observed to gradually decompose meanwhile more thermodynamic stable tubular assemblies grew up little by little (Fig. 9).[61]

The impact of POM clusters on the bulk property of hybrid polymer was further studied with another head-tail PPH. Through directly modifying V_3POM with a trihydroxyl-derived poly(ethylene-glycol) chain, we obtained a head-tail PPH which retains the crystallization behaviour of the PEG block. More interestingly, the incorporation of POM led to a microphase separation in the PEG matrix which results in the hybrid lamellae consisting of alternatively arranged POM and PEG layers. The hybrid lamellae further organized into the spherulitic superstructures that can be intuitively observed by polarizing microscope and TEM. In addition, the strong electrostatic interaction between POM clusters significantly improved the thermostability of such superstructures. As we can directly recognized from the optical photographs that the spherulitic structures were well reserved even at the temperature much higher than the melting point of PEG chain (Fig. 10a).[62] This hierarchical constructing strategy was further developed to design and fabricate new hybrid materials. A bottom-up strategy was applied to tailor the polymer properties. In detail, we blended pure PEG with different amount of the PEG-POM hybrid in aqueous solutions. Then the mixed solutions were allowed to evaporate up the water to give the nanocomposites with different doping proportion. The shear storage moduli of nanocomposites are adjustable over many orders of magnitude at temperatures above the PEG melting point (Fig. 10b). Detailed analysis of TEM results revealed an intriguing evolution of microstructure based on four nano-architectures, which were hybrid self-assembled nanosheets, PEG crystallized lamellae, PEG/hybrid cocrystallized lamellae, and hybrid crystallized lamellae. Because of the strong interaction among POM clusters as well as the good miscibility between the PEG block of the head-tail PPH and the PEG matrix, these nano-architectures can act as nano-enhancers in the material forming process.[63]

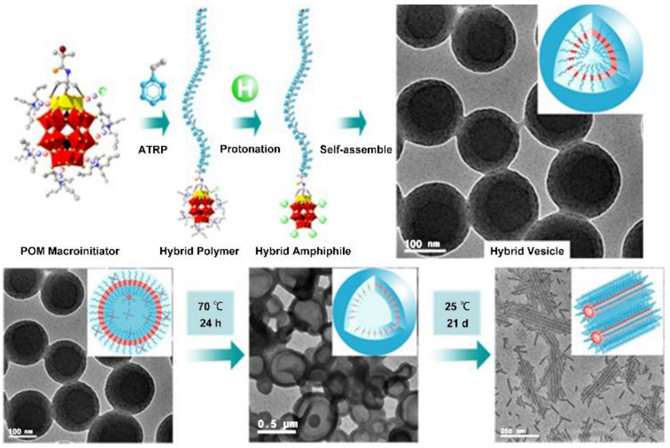

Fig. 9 A molecular model of V_3POM-PS hybrid and schematic demonstration of its self-assembly process.[59-61] Adapted with permissions from Ref.59-61.

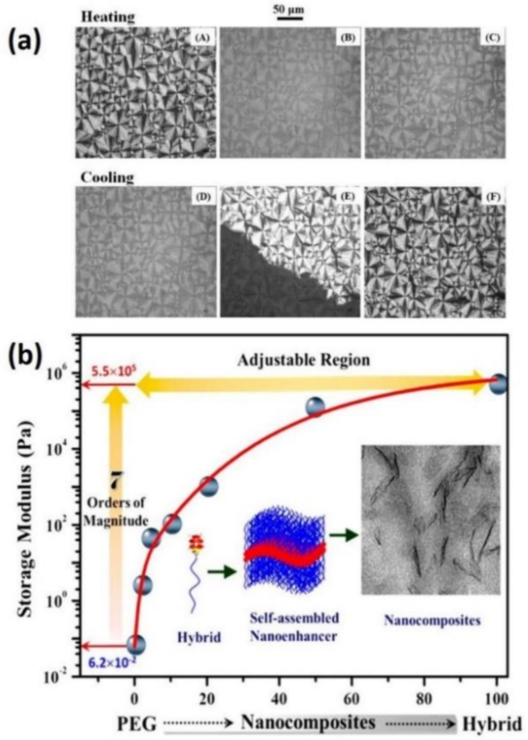

Fig. 10 (a) PLM micrographs demonstrating the strengthening effect stemming from the electrostatic interactions between POM clusters;[62] (b) the hierarchical strategy of self-assembled nano-enhancer to tailor the performance of hybrid nanocomposites.[63] Adapted with permissions from Ref. 62, 63.

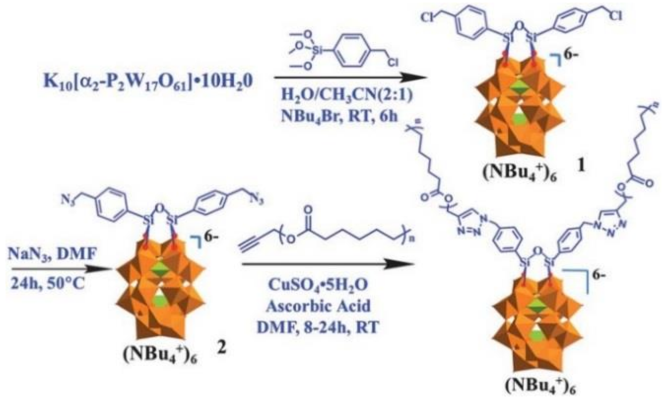

Fig. 11 Schematic representation of preparation of PCL-polytungstate-PCL hybrids via click chemistry.[64] Reproduced from Ref.64 with permission of The Royal Society of Chemistry.

After having general understandings of head-tail PPHs with only one polymer tail, we moved one step further to pursue PPHs with one POM head and two same type polymer tails. We chose copper-catalysed azide–alkyne cycloaddition (CuAAC click), a convenient and efficient method to synthesize such twin-tail PPHs. A monovacant Wells-Dawson polytungstate was chose as the POM head and poly(ε-caprolactone) (PCL) was selected as the polymer tail. As showed in Fig. 11, the monovacant polytungstate was modified by sodium azide to give a bifunctional hybrid cluster, which was white powder and stable in the air. Then the propargyl-terminated PCL chains were quantitatively clicked onto the bifunctional POM to generate well-defined head-tail PPHs. As the resulted PCL-polytungstate-PCL PPHs were freely soluble in THF, the determination of molecular weights and molecular weight distributions were easily carried out on GPC with polystyrene calibration. The molecular weights of PCL-polytungstate-PCL PPHs were almost twice those of PCL precursors and their polydispersity indexes were around 1.1, which were similar to those of PCL precursors. Along with other analysis results, GPC measurement also demonstrated such conventional click chemistry is well adapted to the post-polymerization hybridization of POM.[64]

Among various potential applications of POMs, their potent antiviral, antibacterial and antitumor activities draw permanent attentions. Although there has been reported that POMs show certain curative effect on human disease such as cancers, there is still none of POM-based medicines been developed to clinical experiment. The main obstacle in the exploitation of POM-based medicines is the strong and indiscriminate toxicity of these metal-oxygen clusters. Covalent hybridization with proper organic moieties is considered as a valid way to decrease the toxicity of POMs. Hence we proposed to hybridize the antitumoral Anderson-type polymolybdate by biodegradable and nontoxic PCL chains. The synthesis procedure was carried out by deriving $[\alpha\text{-}Mo_8O_{26}]^{4-}$ cluster using pentaerythritol to obtain a Mn-Anderson hybrid with two hydroxyl groups on each side and then ring opening polymerization was implemented with 4,4'-(dimethylamino)pyridine to activate ε-caprolactone monomers. Four head-tail PPHs were synthesized in quantity with precisely one $[MnMo_6O_{18}]^{3-}$ cluster embedded in the middle. Other than careful confirmation of successful preparation, detailed study was also conducted on the crystallization behaviour and self-assembly in solution of all four PPHs. Generally, crystallization rate decreases with the increase of molecular weight due to the elevation of viscosity and deceleration of chain mobility. However, we found a completely opposite trend in the crystallization process of PCL-polymolybdate-PCL hybrids. We ascribe such abnormal phenomenon to the hindrance of POM clusters, which may aggregate together during the crystallization process and act as crosslinkers or like anchors to delay the movement and rearrangement of polymer chains. These PCL-polymolybdate-PCL hybrids self-assembled into spherical structures in acetonitrile/chloroform ($CHCl_3$: 5 wt%) mixed solvent. As the POM heads were solvophilic, they overspread on the surface of assemblies meanwhile the PCL blocks were piled in the spheres. On the spheres assembled by PCL-polymolybdate-PCL PPHs with shorter polymer chains, we observed multiple concaves on the surface. But those assemblies formed by PCL-polymolybdate-PCL with longer polymer chains all exhibited as solid spheres without any visible concaves. We assume that along with the elongation of polymer chains, the inner space of spherical aggregates was filled up gradually and grown more and more solid, which in turn constructed more rigid assemblies.[65]

Rieger, Hasenknopf, Lacôte and coworkers also make great contributions to the exploration of novel head-tail PPHs with specific focus on thermoresponsive properties. The first thermoresponsive POM-based polymer was prepared by grafting poly(N,N-diethylacrylamide) (PDEAAm), a thermoresponsive polymer, onto an activated organo-derived lacunary heteropolyanion, $\alpha_2\text{-}[P_2W_{17}O_{61}SnCH_2CH_2C(=O)]^{6-}$. Through attacking the mono-oxoacylated polyoxotungstate with primary-amine-terminated polymer chains, an amide post-functionalization method they reported previously, the well-controlled structural characteristics of PDEAAm based on RAFT polymerization was directly inherited by the resulted PDEAAm-polytungstate hybrid. More important, by substituting surrounding ammoniums with the TBA^+ cations, they obtained a water-soluble PPH which exhibited a lower critical solution temperature (LCST) of 38 °C.[66] However this post-polymerization hybridization method inevitably suffers a problem that the achievable length of polymer chain was limited, so they further investigated the possibility of in-situ RAFT polymerization on the same cluster. The organotin-substituted polytungstate was covalently modified by a trithiocarbonate group through click reaction. Analogous to our ATRP procedure, the derived POM $(TBA_7[\alpha_1\text{-}P_2W_{17}O_{61}\{Sn(CH_2)_2C(O)NH(CH_2)_3(N_3C_2H)CH_2OC(O)C(CH_3)_2SC(S)SC_{12}H_{25})$ can serve as a hybrid macroinitiator for RAFT polymerization.[67] Despite the strong oxidative power of POM clusters, there was no profound influence on the RAFT mechanism. A series of head-tail PPHs with PDEAAm chains were synthesized in a controlled way and the length of polymer block can be easily tailored between 10 to 100 kg/mol.

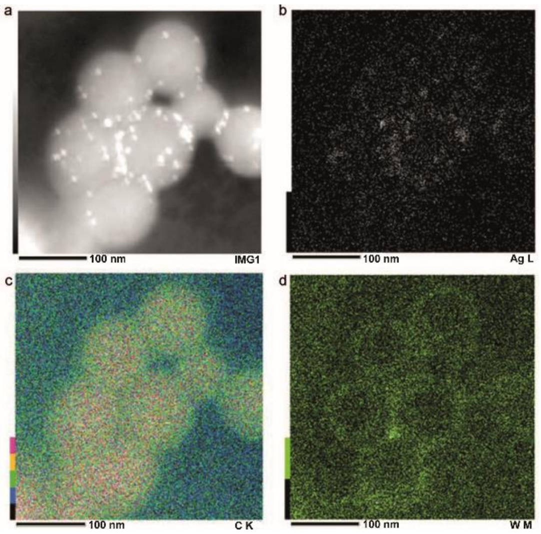

Fig. 12 (a) HAADF image. (b-d) X-ray mapping allowing detection of silver (b), carbon (c), and tungsten (d), realized on the same area as the HAADF image of the PS-polytungstate latex after UV irradiation in the presence of 0.16 mM Ag_2SO_4 and 0.13M propan-2-ol.[68] Reproduced from Ref. 68 with permission from John Wiley and Sons.

In addition, the photocatalytic activity of the parent POM was retained and the synthesis of silver nanoparticles under UV irradiation stated finer and more homogeneous harvest mediated by the resulted hybrids (Fig. 12).[68] The temperature induced phase transition of aqueous solutions of these head-tail PPHs was also studied carefully and revealed a strong influence of POM's counterions on both aggregation mechanism and size.[69] By applying the same POM-based RAFT agent, they further developed a radical emulsion polymerization method to prepare polystyrene-polytungstate composite latexes in water medium. The trithiocarbonate modified organotin-substituted Dawson amphiphile (with ammonium as counterions) played dual roles in the polymerization process, *i.e.* RAFT initiator and emulsion stabilizer. After removing any possible residual POM in serum by four successive centrifugations, the photoactive clusters remained were exclusively located near the surface of PS latexes with covalent attachment. Ag nanoparticles can readily form at the periphery of PS latexes with small and homogeneous sizes compared to other reports. With strong covalent linking, this immobilization strategy not only prevents possible leakage of POM units but also recycles supported catalysts conveniently in aqueous medium.

We can conclude that the head-tail type PPH is the most controllable PPH considering whether the synthetic strategy or the final molecular structure. The well-defined structures and straightforward synthetic routes endow head-tail PPHs with unrivalled superiority in fabricating hierarchical functional materials based on bottom-up strategy. Thinking of the works done by Pradeep and coworkers, in retrospect, if they adopted precisely synthesized head-tail PPHs instead of arbitrarily hybridized materials, the final result would be more solid and convincing. The future research on head-tail PPHs will still concentrate on their fascinating self-assembling behaviours and their applications in micro/nano device design and fabrication. In order to enrich the library of 2D or 3D structures formed by head-tail PPHs, further exploration on constructing novel head-tail PPHs with different polymer tails or block copolymer tails is predictably necessary.

Conclusions and perspectives

This review has almost entirely summarized all the works on polymer-POM hybrids with covalent linking between inorganic POM clusters and organic polymer chains. Successful examples of all four types of PPHs are still limited. During the last decades, indeed, the research was mainly focused on non-covalent organic-inorganic POM hybrids. On the other hand, the intrinsic properties of POMs like strong electronic effect and steric hindrance tremendously impede the pursuit of covalent modification of these versatile clusters.

Although arbitrary and simple approach of blending POM clusters with organic components can satisfy basic functional demands, the latent leakage of toxic heavy metals and macroscopic phase separation are inevitable in non-covalent modification and processing. Meanwhile, the development of covalent modification methods allows us to design and construct more complex and sophisticated organic-inorganic hybrids based on POMs. On the aspect of covalent-building PPHs, we also witness the advance in the synthetic methods from arbitrary radical polymerization to well-controllable ATRP, RAFT and ROMP. Likewise, the configuration of PPH chains evolves from random or linear/branched mixture to well-defined homopolymers or block copolymers. The material performance on photochromics, photovoltaics, catalysis and so on has been preliminarily studied in several covalent PPHs. Maybe the outcomes or efficiencies of these hybrid materials have not reached a dramatic level, the underlying ideas and creativity to produce novel materials are still more than inspiring.

In the next few years, we anticipate a blooming of fabricating and studying covalent-based PPHs. Following the development of covalent modification strategies of POMs, we have enough confidence to predict that more and more kinds of POMs will be integrated in novel PPHs. Especially those PPHs containing POMs with larger sizes and multiple modification sites, there may be some unexpected changes in the final functionalities. On the other hand, as we are growing familiar with POM's impact on the preparation progress and overall functionality, more detailed and accurate design of PPHs will be feasible. Considering that novel advanced materials are mostly fabricated through bottom-up approach, it is natural to conclude that well-defined structure is of significant importance to the overall performance of PPHs. Hence detailed restudy in the existing PPHs from the aspect of molecular structure and manufacturing process (like the solvent effects) will be interesting. Besides, synthesizing more complicated PPHs with diverse organic blocks or other functional polymeric components by applying available polymerization or hybridization methods will never stop and we particularly look forward to the precisely designed and synthesized block copolymers by utilizing ROMP. Other than controlling and improving the molecular structure of PPHs, attention paid on the final functions should be raised too. We should always keep in mind that the ultimate goal of designing and fabricating PPHs with complex structures is to achieve novel hybrid materials with promoted performances or new functions stemming from synergistic effect.

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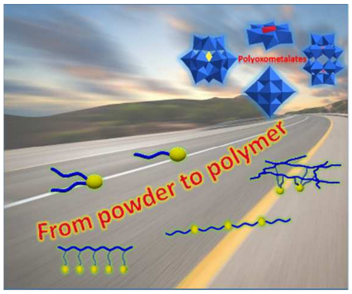

In this Perspective, the field of covalent polyoxometalate-polymer hybrids has been reviewed and some perspectives are provided.