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Synthesis of Functional Poly(disubstituted acetylene)s through the Post-Polymerization Modification Route

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ABSTRACT: We report the recent progress in the preparation of functional poly(disubstituted acetylene)s (PDSAs) through post-polymerization modification routes. The metathesis polymerization of disubstituted acetylene monomers activated by Mo/W–Sn complex catalysts, which do not tolerate highly polar functionalities, was assumed to be a key step in the polymer synthetic procedures. We and other groups have explored several approaches to prepare PDSAs with latent reactive functionalities, which are inactive to Mo/W–Sn complex catalysts but can be used as highly reactive sites for post-polymerization modification. Click chemistry, Michael-type addition reactions, the use of activated esters and other strategies are demonstrated by recently published examples. These works indicate that post-polymerization modification is an efficient route to the synthesis of various functional PDSAs.

Keywords: click chemistry, conjugation, polyacetylenes, polymers, post-polymerization modification

Introduction

Polyacetylene is the archetypal conjugated polymer,^[1] and its substituted derivatives have shown potential applications in electronic materials, liquid crystals, gas permeation, and composites with carbon nanotubes. Great attention has been paid to the design and synthesis of functional polyacetylenes.^[2] The polymerization of monosubstituted acetylenic monomers was greatly facilitated by the development of Rh-based catalysts,^[2f–h,3] which are tolerant to various polar functional groups in the monomers and different solvents; thus, a series of functional poly(monosubstituted acetylene)s (PMSAs), such as poly(phenylacetylene)s, poly(1-alkyne)s, poly(propiolate)s,

and poly(*N*-propargylamide)s, have been successfully prepared.^[2–7] Polyacetylenes (PAs) derived from the polymerization of disubstituted acetylenes, or poly(disubstituted acetylene)s (PDSAs), have shown superior properties such as thermal stability and light emission compared to their PMSA counterparts.^[8] However, the synthesis of PDSAs through the direct polymerization route has proven to be difficult, as functional groups with polarity and coordination capacity tend to poison the early transition-metal-based metathesis catalyst systems. Consequently, only a few kinds of disubstituted acetylenic monomers have been successfully polymerized.^[2,3] The

development of facile and generally applicable synthetic routes toward PDSAs is still a challenging task.

Post-polymerization modification represents an alternative route to synthesize functional PDSAs. With the increasing number of chemical tools in the modern synthetic toolbox, such as the CuAAC reaction, the thiol–ene addition reaction, the use of activated esters, and the Michael addition reaction, post-polymerization modification has become a broad platform for the preparation of diversely functionalized polymers. In this Personal Account, we demonstrate the research efforts to achieve a series of functional PDSAs through the post-polymerization modification route.

Click Chemistry Route

The Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) reaction between azides and alkynes is referred to as “click chemistry”.^[9] Reactions classified as “click chemistry” have the advantages of high efficiency, quantitative yield, mild reaction conditions, and being free of byproducts. CuAAC

reactions have been widely used in the preparation of functional polymers and in the post-polymerization modifications of azide- or alkyne-containing polymers. Some tutorial reviews provide comprehensive information on the relevant topics.^[10]

The first report of using the alkyne–azide click reaction to prepare functional polyacetylenes was contributed by Li and colleagues.^[11a] Recently, we tried to prepare functional PDSAs by taking advantage of the CuAAC method.^[11b] As shown in Scheme 1, the final functional PDSA (P3) was derived through a two-step post-polymerization modification process. The starting monomer (M1) had two triple bonds, but the one protected with trimethylsilyl (TMS) was inactive to the $\text{WCl}_6\text{--Ph}_4\text{Sn}$ catalyst. As a result, the polymerization of this monomer could only lead to the formation of TMS-protected PDSA (P1). Removal of the TMS group gave the ethynyl-functionalized PDSA P2, which could be modified to the target PDSA P3 via the CuAAC route. According to the structural characterization data, the transformations from P1 to P2 and then to P3 were complete, due to the high efficiency and quantitative characteristics of the TMS removal and CuAAC

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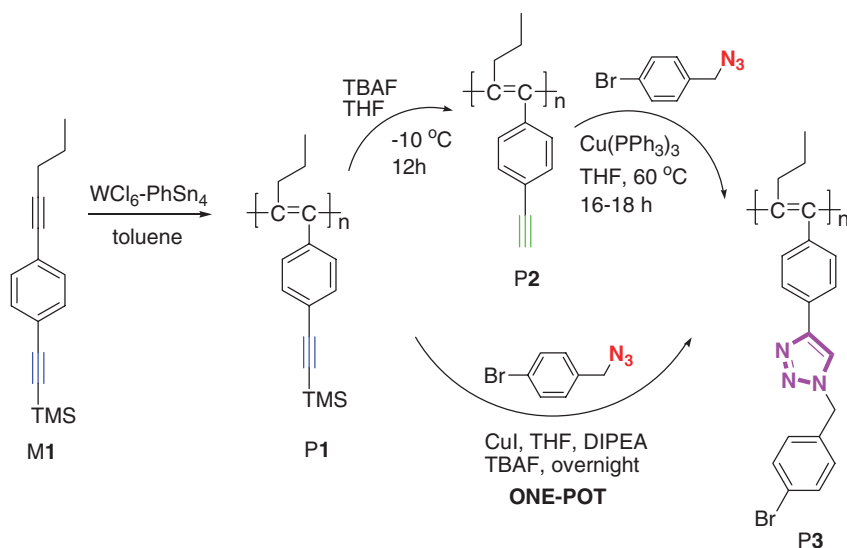


Jing Zhi Sun received his B.S. and Ph.D. degrees from the Department of Chemistry at Jilin University in 1986 and 1999, respectively. He conducted his postdoctoral research at Zhejiang University (ZJU) and joined the Department of Polymer Science and Engineering at ZJU in 2001 as an assistant professor, then became a full professor in 2006. His current research interests include conjugated polymers, polymer hybrids and bioelectronics based on aggregation-induced emission luminogens.



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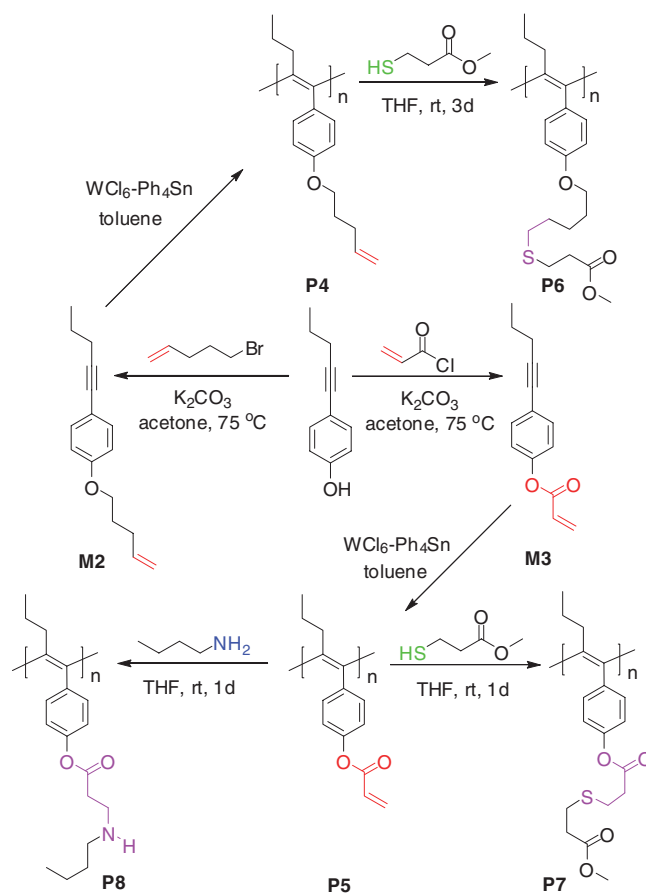


Scheme 1. Post-polymerization modification strategy to synthesize functional PDSAs via alkyne-azide click chemistry.

reactions. Considering that both steps proceeded under mild conditions and the deprotection reaction byproducts had no side effect on the CuAAC process, we tried the “one-pot” synthetic route to **P3** as illustrated in Scheme 1, and the experimental results of this route were similar to those of the two-step reaction. The final product contains bromophenyl moieties, which can be used as reactive sites for further chemical modification.

Michael addition reactions have found applications in the preparation of side chain functional polymers.^[12] Acrylates, maleimides, and vinyl sulfones are frequently used Michael-type reagents. For example, the thiol-ene Michael addition can proceed quantitatively, orthogonally and smoothly in both aqueous and organic media at room temperature; thus, it can also be referred to as a “click reaction”. Different functional polymers have been obtained by using the Michael-type post-polymerization modification strategy.^[13]

We recently explored the feasibility of using Michael addition reactions to prepare functional PDSAs through post-polymerization modification.^[14] The structures and synthetic routes to the precursor PDSAs (**P4** and **P5**) and resultant PDSAs (**P6**, **P7** and **P8**) are displayed in Scheme 2. Disubstituted acetylenes bearing vinyl end groups (**M2** and **M3**) were synthesized and then polymerized using the WCl_6 - Ph_4Sn complex as catalyst. The chemical structures of these polymers were carefully characterized by standard spectroscopic methods and the collected data indicated that the expected PDSAs were obtained in high yields. Both **P4** and **P5** have reactive vinyl groups on their side chains and could thus be used as precursors for subsequent modification with a mercapto compound through the thiol-ene click reaction to afford **P6** and **P7**. The post-polymerization modification of **P4** to **P6** took a long



Scheme 2. Post-polymerization modification route to functional PDSAs via thiol-ene click and Michael-type addition reactions.

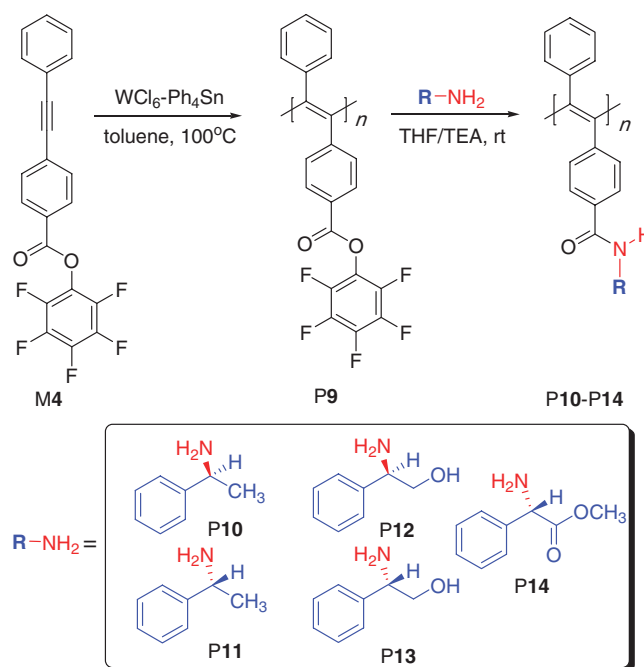
reaction time (three days), because the ene functionality at the end of the P4 side chain links to a saturated alkyl segment. However, when an activated ene functionality (α,β -unsaturated vinyl) was present, as in the conversion of P5 to P7, the reaction required only one day under mild conditions.

Moreover, the activated ene group allowed the post-polymerization modification of P5 via other Michael-type additions, as demonstrated using butylamine as a representative amine compound, with the characterization data confirming the production of the expected P8. It was found that the modified polymers P6 to P8 were fluorescent and showed similar emission efficiency to their precursors P4 and P5. These results indicated that the thiol-ene click reaction and Michael addition reaction are accessible routes for post-polymerization modification to generate novel functional PDSAs.

Activated Ester Route

The first investigation into the preparation of functional polyacetylenes through the activated ester route was reported in 2011 by P. Theato and co-workers.^[15] They prepared four different 4-ethynylbenzoate esters, including the activated ester perfluorophenyl (PFP) 4-ethynylbenzoate. Under the catalysis of the $\text{WCl}_6\text{-Ph}_4\text{Sn}$ complex, both the homopolymerization of perfluorophenyl 4-ethynylbenzoate and the copolymerization of perfluorophenyl 4-ethynylbenzoate with the other three monomers gave rise to high-molecular-weight products. The characterization data indicated that the pendent perfluorophenyl moieties on the homopolymer/copolymers could be thoroughly substituted by primary amines in the presence of triethylamine to give rise to the corresponding amides. The transformation from ester to amide was shown to be quantitative and efficient under mild reaction conditions.

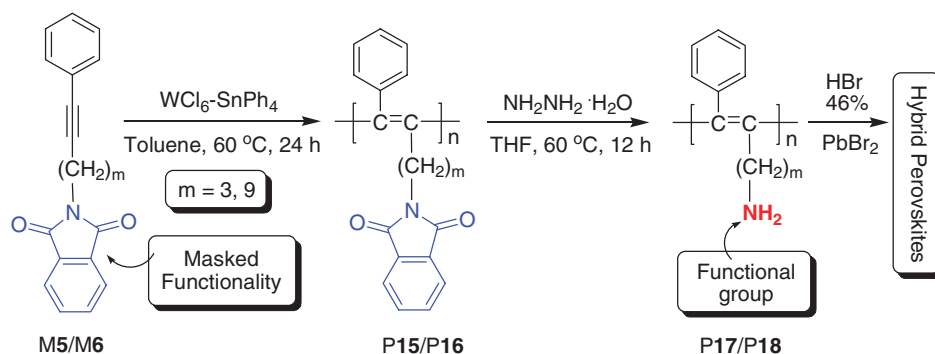
Recently, the authors extended their work to the polymerization of perfluorophenyl 2-ethynylbenzoate, perfluorophenyl 3-ethynylbenzoate and perfluorophenyl 4-ethynylbenzoate, and found that all of these monomers could be efficiently polymerized under the catalysis of the $\text{WCl}_6\text{-Ph}_4\text{Sn}$ complex; in contrast, an Rh-based catalyst only effectively initiated the polymerization of the 2- and 4-isomers and failed for perfluorophenyl 3-ethynylbenzoate. In addition, the configuration of the polyene main chain was *trans*-rich when the $\text{WCl}_6\text{-Ph}_4\text{Sn}$ complex was used as polymerization catalyst, while a *cis*-rich main chain configuration was obtained when the Rh-based catalyst was used.^[16] This trend for the configuration of the polyene main chain was observed regardless of whether the perfluorophenyl ethynylbenzoate had the *ortho*, *meta* or *para* substitution pattern. We used this facile synthetic route to poly(phenylacetylene)s with tunable structures and properties, including the induced circular dichroism of the polyene main chain and the ratio of hydrophobic and hydrophilic side chains.^[17] It has been proven that this strategy



Scheme 3. Post-polymerization modification to synthesize functional PDSAs via the activated ester route.

to prepare functional polyacetylenes through post-polymerization modification is highly efficient.

We applied this strategy to the preparation of PDSAs. As shown in Scheme 3, using chiral amines and amino acids as examples, we demonstrated that post-polymerization modification of activated esters is a facile synthetic route to functional PDSAs bearing highly polar groups.^[18] An activated ester based on diphenylacetylene was designed and polymerized to obtain PFP-activated PDSA (P9). P9 was used as a maternal polymer to further react separately with a diverse range of amines, giving rise to a series of functional PDSAs with chiral moieties and hydroxyl or carboxyl groups. As in the case of PMSAs, the functional PDSAs were derived in high yields under mild reaction conditions. Spectral characterization data indicated that the polymer structures were well consistent with the expected results. A significant feature is that the activated ester route imparts some of the intrinsic properties of P9, such as similar molecular weight and polydispersity index, high thermal stability, and fluorescence, to the obtained disubstituted PAs. In addition, CD spectra reveal that substitution of the activated ester with asymmetric amines transfers the chirality to the polyacetylene backbone, and the polymers in solution show distinct helical conformations, for different chiral moieties have different abilities to induce helix formation. Considering that the substitution of activated esters by amines takes place under mild reaction conditions and there is a library of amine compounds, the present work provides a promising strategy for design and synthesis of various functional PDSAs.



Scheme 4. Post-polymerization modification route to the amine-functionalized PDSAs and their hybridization with $PbBr_2$ to derive the perovskite structures.

Deprotection of Masked Functionalities

The first distinguished example of a functional polyacetylene prepared through post-polymerization modification was an amine-functionalized PDSA.^[19] Under acidic conditions, the protonated amine groups coordinate to metal cations such as Cu^{2+} , Zn^{2+} , Sn^{4+} , and Pb^{2+} . As a result, the organic/polymeric component is incorporated into the obtained organic–inorganic hybrid perovskite structures. To this end, it is necessary to introduce primary amine functionalities to the termini of the side chains of polyacetylenes. It is easy to synthesize PMSAs bearing primary amine side groups by using a Rh-based catalyst in the polymerization of amine-functionalized monosubstituted acetylenes. However, PMSAs tend to quench the emission of the inorganic component; thus, a suitable PDSA is a preferred candidate for the expected perovskite structures. Unfortunately, the amine-functionalized PDSAs are inaccessible by direct polymerization of the corresponding disubstituted acetylenes due to the poisoning effect of amine groups on the catalyst.

A post-polymerization modification strategy was applied in this case. As shown in Scheme 4, Hua et al. opened a synthetic route to the target PDSA (P17) by the polymerization of disubstituted acetylene monomer (M5), in which the primary amine group was protected as a phthalimide moiety. The phthalimide-protected monomer had no poisoning effect on the WCl_6-Ph_4Sn catalyst, allowing the polymerization to proceed smoothly and the precursor polymer P15 to be obtained with high molecular weight. The final polymer was derived from the post-polymerization reaction of the phthalimide and hydrazine, which released the free amine functionalities from the precursor polymer. By aid of the self-assembly process, layers of PDSA ammonium salt alternate with the layers of corner-sharing lead bromide ($[PbBr_4]^{2-}$) octahedra, and the multilayered perovskite structure was successfully derived.^[19,20]

Before this work, most of the organic components used in the formation of ammonium salt–metal halide perovskites were

nonfunctional groups such as alkyl chains that play a secondary role of merely helping to improve the processability of the hybrids. The integration of the PDSA component, a conjugated polymer, bestowed the hybrids with improved energy transfer efficiency and enhanced light-emitting properties. Based on this success, the authors extended their work to introducing liquid crystal mesogens into the perovskite structure by inserting (4-hydroxy-4-biphenyl)oxy moieties into the amine-functionalized and flexible side chains of poly(1-pentyne)s. The resultant ammonium salt modified polyacetylene/ $[PbBr_4]^{2-}$ hybrids showed good solution processability, higher structural stability and ordering.

Afterwards, Xu et al. conducted a further investigation into the hybrid perovskite constructed with the PDSA ammonium salt and $[PbBr_4]^{2-}$.^[21] In the hybrid, the inorganic framework induced the polymer chains to align in an ordered fashion, which helped to populate the chain segments with long conjugation lengths. The hybrid emitted a blue light ($\lambda_{em} = 457$ nm) in a high quantum yield (62%). In addition to the enhanced electronic conjugation, the layer-by-layer structure segregated the polymer chains and weakened interaction between the layers, which resulted in the efficient energy transfer from the inorganic sheets to the organic layers. The hybrid was stable to normal light illumination, but rapidly bleached upon exposure to high-power UV irradiation, enabling the facile generation of a two-dimensional luminescent photo pattern (Figure 1). The inorganic perovskite framework worked as a photosensitizer for accelerating the bleaching process of the PDSA component.

Other Routes

There are other organic reactions possessing the features of high efficiency, high selectivity, high yield and mild reaction conditions that have received attention and been explored for post-polymerization modification. These reactions have also been used in the preparation of various PDSAs in recent years.

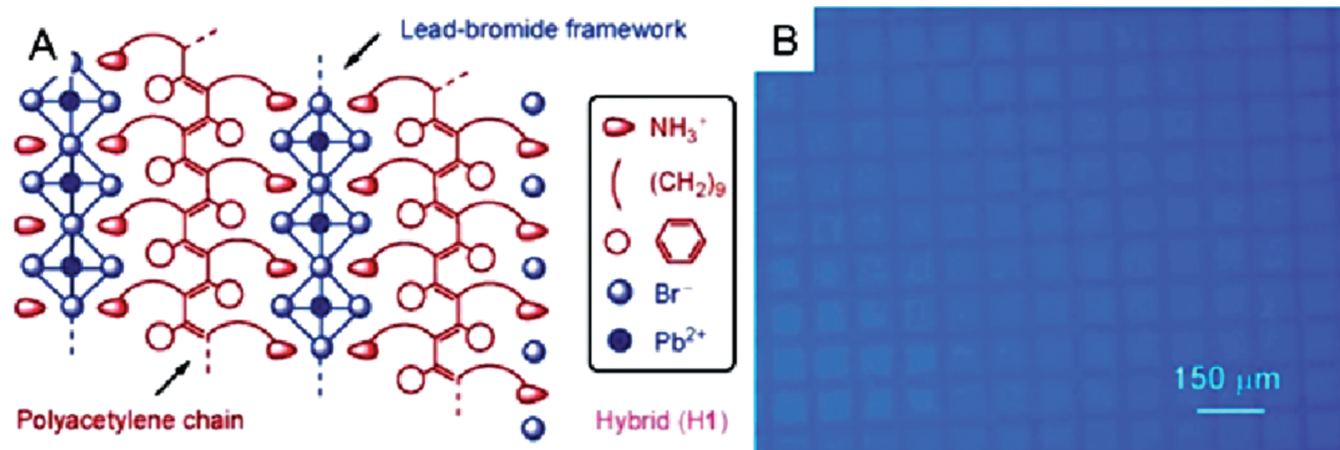
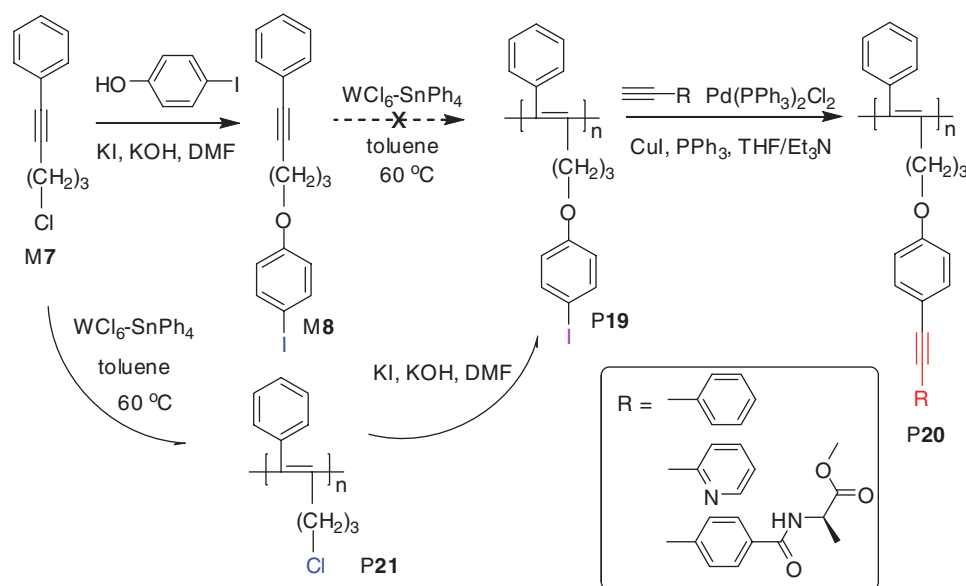


Fig. 1. (A) Illustration of the perovskite structure of amine-functionalized poly(disubstituted acetylene)/PbBr₂ hybrid. (B) Two-dimensional luminescent photo pattern generated by irradiation of a thin film of the hybrid with a UV lamp (365 nm) for 2 min through a copper negative photomask.



Scheme 5. Post-polymerization modification route to target PDSAs via Pd-catalyzed coupling reactions. The precursor PDSA (P19) could not be derived from the direct polymerization of monomer (M8), but could be derived from the intermediate P21. P19 can be further modified by a Pd-catalyzed coupling reaction to the final functional PDSAs (P20).

One such example is the Pd-catalyzed coupling reaction.^[22] As shown in Scheme 5, functional building blocks including pyridine and amino acids were attached onto the PDSA precursor (P19) by Pd-catalyzed coupling reactions between the alkyne and iodoaryl moiety. The Pd catalyst is functionality tolerant; thus, it allows for the modification of the PDSA precursor with highly polar functionalities, which are inaccessible by the direct polymerization of the corresponding monomers. It is notable that the precursor PDSA cannot be simply derived from the

polymerization of the disubstituted acetylene containing an iodoaryl unit, due to the intolerance of the WCl₆-Ph₄Sn catalyst to iodine. This obstacle was surpassed by the substitution of the chlorine atoms on the primary PDSA with 4-iodophenol units (P21 to P19). It is anticipated that many other functionalities could be introduced into the macromolecular structures of the PDSAs by this versatile polymer reaction strategy and that new functionalized PDSAs with novel materials properties could be derived.

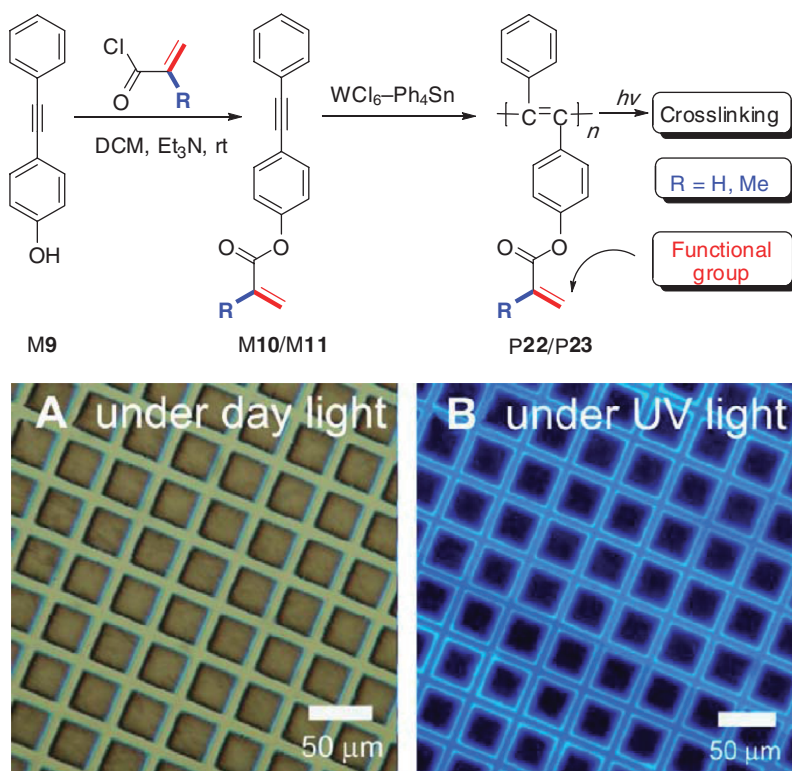


Fig. 2. Post-polymerization modification route to the vinyl-functionalized PDSAs. Three-dimensional negative photoresist images generated by photo-crosslinking of poly(disubstituted acetylene)s containing acrylic functional groups. The photographs were taken under (A) normal room light and (B) a handheld UV lamp for polymer **P23**.

The vinyl in acrylates is a chemically active group and various chemical reactions can take place. Initiator- and photo-/thermally induced polymerization of acrylate-based monomers is one of the best-known polymerizations, while the vulcanization of rubber and the photo-crosslinking of unsaturated resins are the most famous examples of post-polymerization modifications through the reactive vinyl groups and/or carbon–carbon double bonds in the corresponding precursor polymers. Such a strategy has also been employed in the preparation of functional PDSAs. The acrylate moiety was linked to one end of a disubstituted acetylene monomer and, fortunately, the acrylate-functionalized monomer could be polymerized using the $\text{WCl}_6\text{-Ph}_4\text{Sn}$ complex as catalyst (Figure 2) to give rise to a high-molecular-weight polymer. The resulting PDSA emitted strong blue fluorescence in solution and solid films. Under UV light illumination, a [2+2] cyclization reaction took place between the pendent vinyl groups on the PDSA, allowing the development of stable and blue-emitting patterns (Figure 2).^[23]

Yuan et al. reported the preparation and emission properties of acrylate- and methacrylate-functionalized poly(diphenylacetylene)s (Figure 2).^[23] Both **P22** and **P23** emitted efficient green fluorescence in dilute solution. It was

found that the emission spectrum red shifted with increasing polymer concentration. This observation was ascribed to the formation of an intramolecular “exciplex”. In addition, in THF/ H_2O mixtures containing higher volume fractions of water, a unique phenomenon of aggregation-induced emission enhancement was observed and its mechanism was associated with the restricted rotations within the macromolecular chain, which reduced energy dissipation of the excited state by vibrational and rotational processes. Moreover, the vinyl groups in the acrylate/methacrylate moieties were able to undergo [2+2] cyclization addition. As a result, both **P22** and **P23** are promising candidates for the fabrication of fluorescent patterns.

Summary and Outlook

In summary, we have explored the application of a series of post-polymerization modification routes to the synthesis of PDSAs. The alkyne–azide “click” chemical reaction route allows for the post-functionalization of the alkyne-containing precursor PDSA with a variety of azide compounds. Certainly, the alternative route, that is, the post-functionalization of the

azide-containing precursor PDSA with different alkynyl compounds, would also be worthwhile to investigate. This route opens a way to attach a series of functional groups to the PDSA via a triazole linkage, if the azide group does not harm the polymerization catalysts of disubstituted acetylenes. The thiol-ene click reaction has also been used in the preparation of functional PDSAs through the post-polymerization modification route. This strategy has proved to be highly efficient when the activated vinyl was used as an ene moiety, and reactive and highly polar functionalities can be introduced into PDSAs by properly modified thiols. It would be rational to further extend this to other thiol-ene click chemistry methods with activated C=C double bonds.

In addition to the thiol group, primary amines can also react with activated C=C double bonds, which is referred to as a Michael-type addition reaction. This route allows for grafting of different functional groups to the precursor PDSAs using various compounds containing primary amines. The use of activated esters is the most accessed route to functional polyacetylenes. It enables both primary and secondary amines to be used as the post-polymerization modification agents, which includes a very large family of organic compounds containing versatile functionalities. As to amines, restoration of the phthalimide-protected amine was used for the preparation of PDSA-PbBr₂ hybrid perovskites. This was the first report of the fabrication of ordered organic-inorganic hybrids from PDSAs, although the synthetic route seems to be long. Considering that it is necessary to incorporate suitable functional groups into PDSAs to achieve strong interaction between organic and inorganic components, other protection strategies need to be explored.

Despite the promising recent progresses, there is still a huge space to open more synthetic routes to PDSAs. To date, only a few chemical groups have been attached onto precursor PDSAs, which include amines (for activated esters and Michael addition), thiols (thiol-ene addition), and azides and alkynes (CuAAC). Other functionalities, such as oxygen-containing groups (e.g., aldehyde, carboxyl, hydroxyl, phenol) will open new avenues to novel functional PDSAs. In this regard, another kind of activated ester, i.e., thiobenzothiazole ester, seems to be promising because the hydroxyl-containing compounds can be applied to the preparation of PDSAs. In addition, aldehyde-amine reactions can be adapted to the preparation of PDSAs through post-polymerization modification routes.

Moreover, some additional efficient coupling reactions are worth attempting. The Pd-catalyzed alkyne-iodine coupling reaction reviewed here is one successful example. Diels-Alder cycloaddition and photo-triggered [2+2] cyclization reactions could be other accessible routes. The obvious challenge is to realize the proper geometry between the construction elements, which is deplorable for cyclization and cycloaddition reactions. To open new applications of PDSAs in electronic and biological

fields, more rigorous challenges await researchers. For example, trace amounts of metal catalysts will be harmful in electronic devices and in biological events. Consequently, it is of great importance to develop alternative routes to PDSAs without using metal catalysts. For biological applications, water solubility is a primary requirement. Thus, it is an important task to design and synthesize some water-soluble PDSAs through suitable post-polymerization modification routes,^[24] since all of the currently available catalysts used for preparing PDSAs are intolerant to hydrophilic chemical groups. Certainly, the post-polymerization modification route is a compensatory scheme due to the absence of strategies to directly obtain desirable functional PDSAs. With the increasing number of available chemical tools in our toolbox, both the post-polymerization modification and direct polymerization routes to functional PDSAs are expected to become smoother and more versatile in the future.

Acknowledgements

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