

Click Polymerization: The Aurora of Polymer Synthetic Methodology

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ABSTRACT: As an emerged efficient polymerization methodology, the click polymerization plays a significant role in the area of polymer and materials sciences. Similar to the click reaction, the click polymerization enjoys the advantages of high efficiency, mild reaction conditions, and high regio- and stereo-selectivity *etc.* In this highlight, we summarize the recent progress on click polymerizations, with focus on the alkyne-based

ones. The challenges and opportunities in this area are also briefly discussed. © 2016 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, 00, 000–000

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INTRODUCTION Nowadays, the polymeric materials have been widely applied in diverse areas. Exploration of powerful and efficient polymerization reactions to facilitate construct polymeric materials with novel structures and advanced properties is an everlasting topic in polymer science. Generally, new polymerization reactions, if not all, are derived from the existing highly efficient organic reactions. Indeed, over the past decades, various efficient organic reactions have been developed into polymerization reactions. One of the well-known examples is the click polymerization, which is exactly derived from the click chemistry.

Click chemistry, conceptually introduced by Sharpless and co-workers in 2001, refers to a new class of organic reactions that enjoy the features of high efficiency, regioselectivity, modularity, atom economy, simple product isolation, functional group tolerance, and so on.¹ The Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC), which was reported in 2002, well meets the characteristic of click chemistry and has been emerged as an archetypal click reaction.² The CuAAC is so efficient, robust and orthogonal that it well satisfies the requirements for an organic reaction to be developed into a polymerization reaction, such as high efficiency, mild reaction conditions, easy access to the catalyst and starting materials.³ Thanks to the tremendous efforts devoted by polymer scientists, the click reaction has indeed been developed into an efficient click polymerization.⁴

Besides sharing the advantages of click reaction, click polymerization also possesses its unique properties, such as easy

access to and facile variation of the monomers, large-scale purification, good solubility of the products, versatile properties.⁵ Contrast to traditional polymerizations, the powerful click polymerization makes it possible to integrate units with different characters, for instance, rigidity and flexibility, topology, polarity, and charge, into one polymeric scaffold.⁶

This highlight intends to interpret the most remarkable progress on the development of click polymerizations. Particular emphasis was put on the development of new polymerization reactions based on triple-bond building blocks, such as the azide-alkyne and thiol-yne click polymerizations. Moreover, the perspectives and challenges in this area are also discussed. Owing to the space limitation, the applications of the resultant polymers, the mechanism aspects of polymerization processes and post-functionalization of preformed polymers are not included in this highlight.

DEVELOPMENT OF CLICK POLYMERIZATIONS

Since the first attempt of using click reaction to prepare polymers in 2004,⁷ the click polymerization has proven to be a new platform for simple and straightforward preparation of polymers with various structures and versatile functions.⁸

Currently, several kinds of click polymerizations have been developed. Among them, the Cu(I)-catalyzed azide and alkyne polycycloaddition, has been established as a powerful and selective method for polymer synthesis.^{4–8} Moreover, the

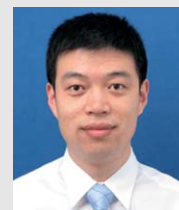
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1,3-dipolar polycycloaddition of nitrile N-oxides and azides has also been developed into a click polymerization.⁹

Another attractive click polymerization is thiol-based one, which is essentially a novel active free-radical polymerization. For instance, the photoinitiated and thermo-induced thiol-ene,¹⁰ thiol-yne click polymerizations,¹¹ and the thiol-epoxy click polymerizations have been reported, from which functional polymers were facilely prepared.¹²

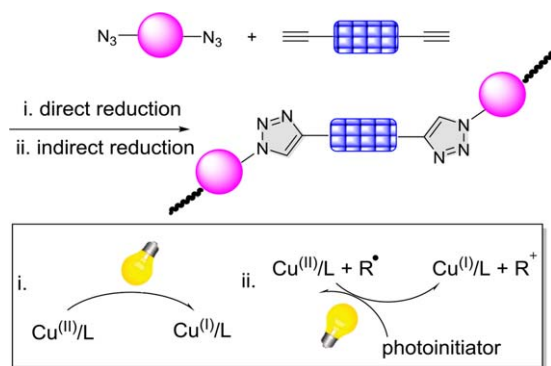
CU(I)-CATALYZED AZIDE-ALKYNE CLICK POLYMERIZATION (CUAACP)

During the past years, the CUAACP has been systematically investigated.³⁻⁶ It has been considered as the most extraordinary polymerization that makes profound impact on a wide range of research areas, including material science and supramolecular chemistry *etc.* Various Cu(I) species were utilized to catalyze the azide-alkyne click polymerization (AACP). The general Cu(I) catalyst was formed by *in situ* reducing Cu(II) ions with sodium ascorbate or metallic copper (Cu).² Meanwhile, the Cu(I) compounds and complexes, like CuBr and Cu(PPh₃)₃Br, were also widely used in the CUAACP.⁴ It should be mentioned that Ru(II) complex of Cp*Ru(PPh₃)₂Cl could also catalyze the AACP.¹³ Different from the CUAACP which produces polytriazoles with 1,4-regioregularity, the Ru(II)-catalyzed AACP readily generates sole 1,5-regioregular polytriazoles.¹³ In addition, microwave assistance¹⁴ and ultrasonic irradiation¹⁵ could be used to accelerate the CUAACP. The external stimuli offer the

polymerizations with additional reaction energy, thus leading to higher efficiency and shorter reaction time.

In recent years, the photoinitiated CUAACPs have emerged as an exciting polymerization method.¹⁶ The key is the generation of Cu(I) species from variable copper sources in direct or indirect pathways under UV irradiation.¹⁷ In a direct photolysis, an intramolecular charge-transfer from the π -system of a ligand to the metal ion was triggered by UV light, resulting in the reduction of Cu(II) to Cu(I) species. However, the direct process requires ligand stabilizer, hence, the indirect method is more effective. The irradiation of visible or UV light on the photoinitiators readily generates electron donor radicals, which facilitates the formation of Cu(I) species. Unlike thermally induced reactions, the photoinitiated system could realize the spatial and temporal control of the polymerizations. Thus, it is a promising process as a controllable click polymerization. (Scheme 1)

The complete removal of the transition-metal residues from the resultant polytriazoles, however, has been proved to be difficult because the metallic residues could coordinate with the nitrogen atoms of the formed triazole rings. The toxicity of the metal residues is the major hazard for applications of polytriazoles in biological field. Moreover, they could also quench the light-emission of the products, which limits their application in optoelectronic field. One alternative to overcome this drawback is to use a supported Cu(I) catalyst. The relatively strong binding of the copper ions to the supporting substrate could reduce metallic residues coordinated to the



SCHEME 1 (i) Direct and (ii) indirect methods of photoinitiated CuAAC.

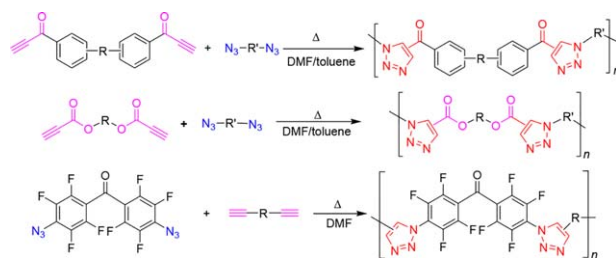
resultant polymers. Meanwhile, the supported Cu(I) catalytic systems could be recycled and reused. Recently, we have reported several examples of recyclable and reusable supported Cu(I) catalysts for the AACPs.¹⁸ For example, a supported catalyst of CuI@A-21 was facilely produced by immobilizing CuI onto a dimethylamino-grafted cross-linked polystyrene (Amberlyst® A-21). The catalyst could effectively catalyze the AACP under mild reaction conditions without other additives and be used for 4 cycles. Due to the less copper residues, the optoelectronic property of polytriazole has been enhanced.

METAL-FREE CLICK POLYMERIZATION (MFCP) OF AZIDE AND ALKYNE

As aforementioned, although the supported Cu(I)-catalyzed AACP could minimize the unfavorable influence of copper residues, the problems caused by them are not able to completely circumvent. Therefore, AACP in the absence of transition-metal catalysts, that is, the MFCP becomes a promising alternative.³

During our research on establishment of new polymerizations based on triple-bond building blocks, we found bis(arylacetylene)s possessed high reactivity. They could be polycyclotrimerized in the presence of secondary amine instead of highly sensitive and active transition metal complexes. By taking the high reactivity of bis(arylacetylene) monomers, the first example of MFCP of activated alkynes of aryloxyalkynes and azides was successfully established (Scheme 2).¹⁹ This MFCP could be carried out in polar solvents such as DMF/toluene mixture at a moderate temperature of 100 °C. Soluble polytriazoles with high weight-average molecular weight (M_w up to 26,700) and regioregularity (the fraction of 1,4-isomers, $F_{1,4}$, up to 92%) could be obtained in high yields (up to 98%).^{19(a)} Importantly, oxygen and moisture exert little effect on this MFCP, which could greatly simplify the polymerization procedures and facilitate the preparation of functional polytriazoles.^{19(b)}

According to the structural similarity of aryloxyalkynes, we also established another MFCP of propiolates and azides.²⁰



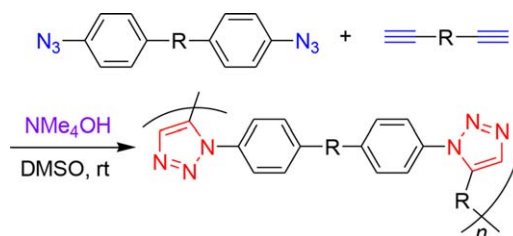
SCHEME 2 MFCPs of alkynes and azides.

More importantly, propiolate monomers could be prepared from commercially available propionic acid and aromatic/aliphatic diols via a one-step esterification under mild conditions in an environmentally benign fashion. The experiments showed that this kind of MFCP could provide similar results with that of MFCP of aryloxyalkynes and azides, which provides even simpler and more efficient tool for the preparation of polytriazoles with diverse structures and versatile properties.

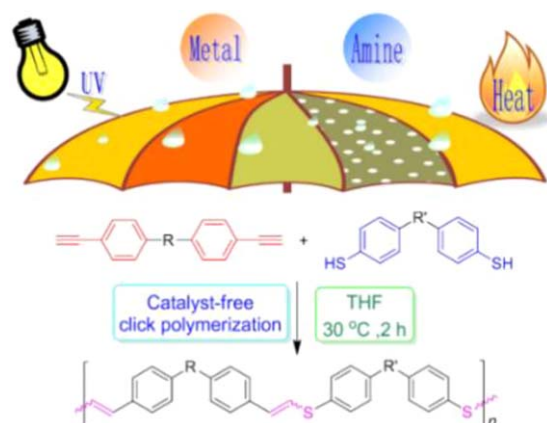
Identically, the activated azides should also facilitate the MFCP. Indeed, the perfluorobenzophenone activated azide was more active than ordinary one, and could remarkably accelerate the polymerization with alkynes.²¹ As a result, the MFCP of activated azide and alkynes was also successfully developed. Polytriazoles with M_w values in the range of 5800–34,000 and high $F_{1,4}$ (82–85%) were obtained in high yields (up to 93.2%).

ORGANIC BASE MEDIATED CLICK POLYMERIZATION OF AZIDES AND ALKYNES

Although great progress has been made in the development of MFCP, the regioregularity of the products is far beyond perfect. To obtain the polytriazoles with 100% regioregularity under metal-free conditions, we paid attention to the organocatalyst systems. In 2015, we successfully established an organic compound mediated AACP. As shown in Scheme 3, aromatic alkynes and azides could undergo the polycycloaddition in the presence of an organocatalyst of tetramethylammonium hydroxide (NMe_4OH) in DMSO at room temperature.²² More importantly, sole 1,5-disubstituted 1,2,3-triazole containing polymers with high M_w values (up to 56,000) were obtained in high yields (up to 96%). Thus, this polymerization could be regarded as a new kind of



SCHEME 3 NMe_4OH -mediated click polymerization of aromatic alkynes and azides.



SCHEME 4 Syntheses of poly(vinylene sulfide)s by catalyst-free thiol-yne click polymerizations of diynes and dithiols. (Reproduced from Ref. 24(a), with permission from American Chemical Society.)

efficient MFCP. It is worthy to note that this NMe_4OH -mediated MFCP provides an alternative tool for the preparation 1,5-regioregular polytriazoles besides the Ru(II) -catalyzed AACP.

THIOL-YNE CLICK POLYMERIZATION

Using thiol-yne click polymerization to synthesize sulfur-containing polymers with topological structures and advanced functions is a hot research topic.^{12,23} In accordance with the reaction mechanism, the thiol-yne click polymerizations could be fell into three major categories: free-radical, amine-mediated and transition-metal catalyzed processes. Thus, UV light, heating, organic bases, or transition metal complexes are indispensable for these kinds of click polymerizations.

The recent works revealed that the thiol-yne click polymerization could be propagated without using additional catalysts and external stimuli. Simply mixing the aromatic diynes and dithiols with equivalent molar ratio in THF at 30 °C and reacting as short as 2 h, soluble and regio-regular functional PVSs with high molecular weights (M_w up to 85,200) were readily produced in excellent yields (up to 97%; Scheme 4).²⁴ Thus, this polymerization undergoes via a spontaneous fashion. The mechanism investigation revealed that this polymerization propagated via a free-radical process. This established new click polymerization enables us to succinctly synthesize PVSs with different architectures and multifunctional properties, such as high refractive index values and aggregation-induced emission.

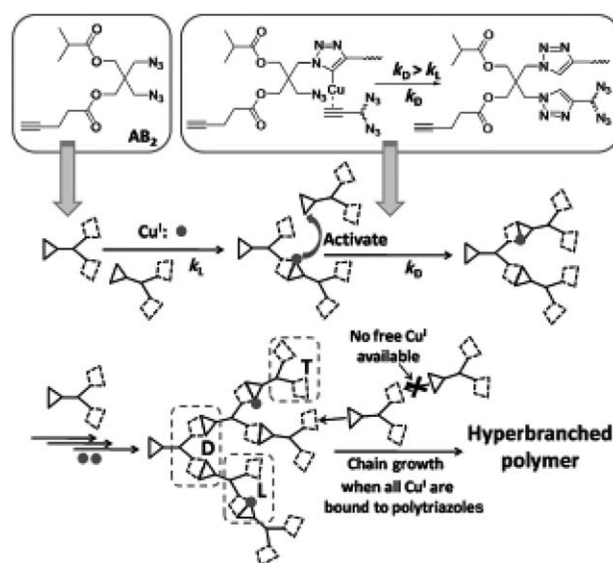
PERSPECTIVES OF CLICK POLYMERIZATION

Despite impressive progresses have been made on the click polymerizations, the study on them is still worthy unremitting efforts. The area is full of challenges, which also means tremendous opportunities. First of all, new types of click polymerizations are still highly desired for they could produce polymers with new architectures and novel functions. For example, the newly reported amino-yne click polymerization

is a promising candidate to be used to facilely prepare nitrogen-containing polymers.²⁵ Moreover, new click polymerizations could be developed based on newly reported efficient organic reactions. However, carbon-nitrogen triple-bonds based click polymerization is another attracting research direction because the organic reactions have been reported. For example, the azide-acetonitrile click reaction was reported and 5-amino-1,2,3-triazoles could be generated.²⁶ In addition, a new highly efficient silver catalyzed click reaction of terminal alkynes and isocyanides was presented in the literature.²⁷ Thanks to their high efficiency and mild reaction conditions, they are hopeful to be developed into new kinds of click polymerizations.

Secondly, the controlled click polymerization processes are also challengeable. Controlled polymerization is of vital importance for the design and synthesis of polymers with controlled degree of polymerization and narrow polydispersity as well as well-defined structures. However, the controlled click polymerization is rarely reported due to its step polymerization nature. The progress on this aspect was made by Gao *et al.* recently. They reported that CuAACP could perform via a “chain polymerization” manner.²⁸ The use of a AB_2 monomer and diminishing the amount of Cu(I) catalyst are the key issues to ensure the AACP to display the feature of a “living” chain-growth mechanism and to produce hyperbranched polytriazoles with a narrow polydispersity (<1.3 ; Scheme 5).

Gao’s work shines light on the development of controllable click polymerizations through systematically surveying the catalysts and monomers. For example, the spontaneous thiol-yne click polymerization, which performs with a free-radical process, is promising to be developed into a controlled click



SCHEME 5 Synthesis of hyperbranched polymers with low polydispersity and a high degree of branching by chain-growth CuAACP. (Reproduced from Ref. 27, with permission from Wiley-VCH Verlag GmbH & Co. KGaA.)

polymerization. Moreover, the photoinitiated AACP could give access to spatial and temporal controls of the polymerization procedure and polymer structures.

Thirdly, thanks to their robust and orthogonal nature, the click polymerization provides a powerful and efficient tool for the preparation of polymers with multifunctional properties, such as aggregation-induced emission,^{19(b)} self-healing,²⁹ optical nonlinearity,³⁰ and high refractive index.³¹ However, the full potential of the polymers are far beyond explored. For example, the property of triazole units in the polytriazoles has not been fully realized. Furthermore, the click polymerization also shows infinite opportunities in the areas of shape-memory materials, drug delivery, conjugated porous materials, biologically compatible fibers, and so forth. We fully believe that the click polymerization will sparkle in the preparation of functional materials though it is in the infancy stage.

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