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Activated Internal Alkyne-Based Polymerization

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Comprehensive Summary

As an emerging and efficient polymerization methodology, activated internal alkyne-based polymerization has been considered as a powerful tool for the construction of polymers with diverse architectures and versatile functions. This review focuses on the recent progresses in the polymerization using mono-activated, di-activated, in-situ generated, ring-strained ethynyl groups as substrates, coupling with post-modification on premade polymers containing activated internal ethynyl groups. Representative examples are used to illustrate the fundamental design strategy, the development of polymerization and post-functionalization, along with the properties and potential applications of the prepared polymers. Moreover, the challenges and perspectives in terms of new-type active alkynes, green polymerization methodology, tailored regio-/stereoselectivity modulation, and potentially expanded application in this area are also discussed.



Keywords

Activated internal alkyne | Polymerization | Functional polymer | Post-functionalization | Property and application

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Left to Right: Author 1, Author 2, Author 3

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1. Introduction

Alkynes, a general term for compounds with carbon-carbon triple bonds, are another building block in synthetic polymer chemistry beyond alkene and arene substances.^[1–3] Although the alkyne-based polymerizations are rarely described in the textbooks, plenty of polymers with diverse structures and versatile functionalities can be synthesized and derived from alkyne monomers, attracting avid attention from different academic research communities such as polymer chemistry, biochemistry, materials science and so on.^[4–14] Nevertheless, alkyne-based polymerizations are still limited in applications and confront challenges to some extent, owing to the poor reactivity of the ethynyl groups. Thus, much effort has been devoted to improve the reactivity of alkynes by a adjacently connecting electron-withdrawing groups, which is colloquially termed as the activated alkynes. Featuring with superior reactivity and extensive variation, activated alkyne-based polymerizations have been widely used to construct functional polymers with desired structures and are regarded as reliable and powerful means in the toolbox of chemists.^[15–18]

Activated internal alkynes not only inherit the unique characteristics of activated analogues but also enable the polymeric materials with structural enrichment and application expansion. Over the past decade, polymer chemists and material scientists have combined efforts to develop the conspicuous polymerization and post-polymerization modification based on activated internal alkynes and to explore the functionalities and applications of the resultant materials. The prosperity of activated internal alkyne-based polymerizations always call for the inspiration and devotion in view of our fundamental comprehension about this realm. Herein, we attempt to overview the evolution of a activated internal alkyne-based polymerization and post-functionalization strategies. Therefore, the representative examples in each category are introduced in detail, whilst guiding the readers to the important advances and key developments. Moreover, the challenges and perspectives in this area are also briefly discussed.

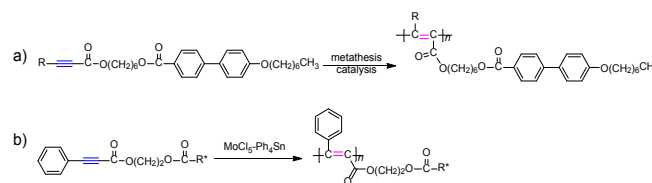
2. Polymerization of Mono-Activated Internal alkynes

2.1. Metathesis polymerization

Polyacetylene (PA) is a Nobel Prize-winning conductive polymer. Replacement of a hydrogen in polyene backbone can not only help tackle the notorious intractability and instability but also generate new substituted PA derivatives with latent properties.^[19,20] An impressive example of the polymerization of disubstituted activated acetylene was contributed by Tang and coworkers in 2002.^[21] The disubstituted propiolates were effectively polymerized by the classic Mo- and Rh-based catalysts for the synthesis of polypropiolates with high weight-average molecular weights (M_w , up to 353600) (Scheme 1a). The electronic and steric interactions of the propiolic carbonyloxy group with the polyene double bond endowed polymers with thermal stability. Some polypropiolates with special liq-

uid crystallinity and luminescence behavior are promising candidates for the polarized light materials in the construction of optical display system. To further prove the versatility of this propiolate system, Tang and coworkers also prepared the helical poly(alkyl phenylpropiolate)s bearing stereogenic pendants, whose optical activity could be tuned by external stimuli to some extents (Scheme 1b).^[22]

Scheme 1 Synthesis of polyacetylenes by metathesis polymerizations.



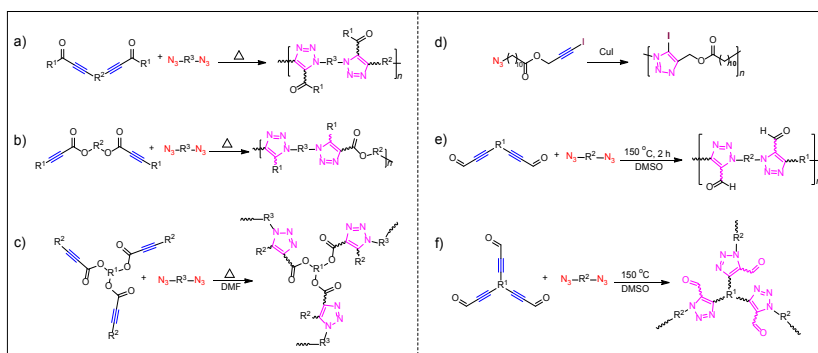
2.2. Azide-activated internal alkyne polycycloaddition

Transition metal-catalyzed azide-alkyne click polymerization has been widely used for the preparation of polytriazoles (PTAs) with topological architectures and advanced functions.^[23] However, the residue metallic residues are detrimental to the optoelectronic property and biocompatibility of the products. The most effective way to circumvent this issue is to develop metal-free click polymerization.^[15,16] Inspired by the polymerization reactions using active arylacetylene,^[24] Qin, Tang and coworkers further established an efficient metal-free polycycloaddition of diazides and carbonyl-activated internal alkynes, from which soluble and thermally stable 1,4,5-trisubstituted PTAs with high regioregularity (up to 74%) and M_w (up to 16400) were furnished in satisfactory yields (up to 99%) (Scheme 2a). Thanks to the benzoyltriazole units, the polymers possessed high refractive indices and could generate 3D photopatterns, making them promising in microelectronic device applications.^[25] In addition, Moszner, Schubert and coworkers adopted neat polymerization of analogous internal alkynes and multifunctional azides to generate multiple hard materials with a maximum E -modulus of 2.5 GPa. Given the good mechanical performance and absence of catalyst residue, these polymers open a great prospect for biology and medicine applications.^[26]

To avoid the harsh synthetic conditions for the internal arylacetylene, ester-activated internal alkynes have been designed and used to react with azide monomers (Scheme 2b).^[27–29] For example, Li, Tang and coworkers developed a metal-free phenylpropiolate-azide polycycloaddition, which was performed smoothly at 150 °C in *N,N*-dimethylformamide (DMF), and regioregular poly(phenyltriazolylcarboxylate)s with high M_w (up to 28500) were produced in high yields (up to 98%) in 4 h. The tetraphenylethene (TPE)-containing polyester exhibited unique aggregation-induced emission (AIE) characteristic,^[30] which could be applied in the areas of explosive detection and fluorescent pattern.^[28] To make the polymerization process more environment-friendly, they further established a solvent- and catalyst-free butynoate-azide polycycloaddition in a regioselective fashion, generating soluble poly(methyltriazolylcarboxylate)s with high M_w (up to 16700) in high yields (up to 90%). In addition, poly(1,2,3-triazolium)s were also prepared and explored their application in cell-imaging.^[31] With these efficient cycloaddition polymerization tools in hand, TPE- and ferrocene-based hyperbranched PTAs with versatile properties such as AIE feature, electrochemical activity, and thermal stability, have been easily synthesized and applied in nitroaromatic detection and fabrication of fluorescent pattern and nanostructured magnetoceramics (Scheme 2c), etc.^[32–34]

To further complement and expand the multiplicity of triazole-

Scheme 2 Synthesis of linear and hyperbranched polytriazoles by azide-activated internal alkyne polycycloadditions.



based materials, Fokin and coworkers reported a novel step-growth click polymerization of α -azido- ω -iodoalkyne monomer in the presence of Cu(I) catalyst and amine ligand (Scheme 2d). This iodoalkyne exhibited enhanced reactivity toward azide during polymerization, furnishing structurally diverse poly(5-iodo-1,2,3-triazole) with high M_w (up to 49200) and good solubility. Taking advantage of the iodine unit at 5-position of the triazole ring, the resultant polymer could be further functionalized to generate plentiful PTAs with individual properties through metal-catalyzed coupling reactions.^[35]

Recently, facilely post-functionalizable poly(formyl-1,2,3-triazole)s were reported by Qin, Tang and coworkers using an efficient metal-free polycycloaddition with aldehyde-activated internal diynes as monomers (Scheme 2e). Plenty of soluble and thermally stable formyl-PTAs with high M_w (up to 54600) were produced in high yields (up to 93%) and a regiospecific manner (up to 71%) at 150 °C in dimethylsulfoxide (DMSO) after 2 h. Notably, bearing high reactivity of the aldehyde groups, the resultant polymers could serve as a fluorescent probe for selective detection of hydrazine and function as a valuable platform for further functionalization of PTAs with distinct thermal and optical properties.^[36] Using this elegant azide-alkyne polymerization technique, a series of hyperbranched formyl-PTAs with satisfactory M_w (up to 26400, $M_{w, \text{MALLS}}$ up to 660200) were prepared in moderate yields (up to 84%) by Qin, Tang and coworkers (Scheme 2f). Owing to the excellent functional group tolerance, triphenylamine and binaphthyl moieties could be facilely incorporated into the polymers to endow them with fluorescence and circular dichroism properties, respectively. Thanks to the large amount of activated ethynyl and aldehyde units on their peripheries and in the internal branch chains, the resultant polymers can undergo efficient single-/double-stage post-functionalization via azide-alkyne cycloaddition and Knoevenagel condensation reactions. In particular, quadruple-modal information encryption and storage with enhanced security and density were achieved based on the extraordinary fluorescence responses to hydrazine and hydrochloric acid of the hyperbranched polymers.^[37]

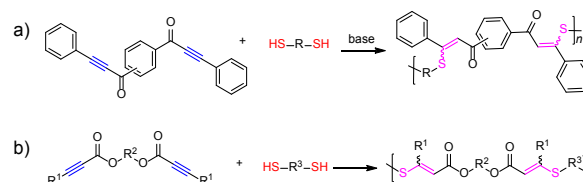
2.3. Thiol-yne polymerization

Sulfur-containing polymers that featured numerous fascinating properties such as thermal stability, high refractivity, metal coordination ability, remarkable dielectrical and electrochemical properties have been found great potential applications as optical and optoelectronic materials.^[38-41] As a result, the synthesis and property of sulfur-containing polymers have drawn increasing attentions from the academic and industrial communities. A precursive attempt to prepare poly(enonsulfide)s with good mechanical and thermal performance by nucleophilic addition polymerization of activated dipropynones with aromatic dithiols was reported by Bass

and coworkers in 1987 (Scheme 3a).^[42] Interestingly, the stereoregularity of polymers could be fine-tuned via the reaction solvent and base catalyst. Coincidentally, Dix and coworkers explored a similar polyaddition reaction between dithiothreitol and bis(acetylene ketone) in the presence of triethylamine, and poly(enone-sulfide) with 60% Z-isomer and moderate molecular weight was yielded, which might be used as a curing system for paint, coating or adhesive.^[43]

In order to foster the polymerization between activated internal alkyne and thiol as an efficient tool for the construction of functional polymers, it is necessary to expand the scope of active alkyne monomers, such as ester-activated internal alkynes (Scheme 3b). In 1995, Endo and coworkers reported a $n\text{-Bu}_3\text{P}$ -catalyzed polyaddition of bis(propiolate)s with dithiols, and polymers bearing β -alkylmercaptoenolate moieties with high number-average molecular weights (M_n , up to 26400) were obtained in excellent yields (up to 95%). Notably, some polymers exhibited good film-forming ability and high refractive indices, offering them promising application in the realm of optical materials.^[44] Recently, butynoates and phenylpropiolates have been used to react with dithiol substrates under catalyst-free conditions. This thiol-yne click polymerizations were readily performed in DMF at 60 °C, furnishing poly(β -thioacrylate)s with satisfying M_w (up to 50300) and stereoregularity (Z isomer up to 84%) in high yields (up to 91%) after 24 h. Integration of good optical transparency, high refractive indices with low chromatic dispersions, and AIE feature within the resultant poly(β -thioacrylate)s are therefore anticipated to be brand-new functional polymers for high-tech applications.^[45]

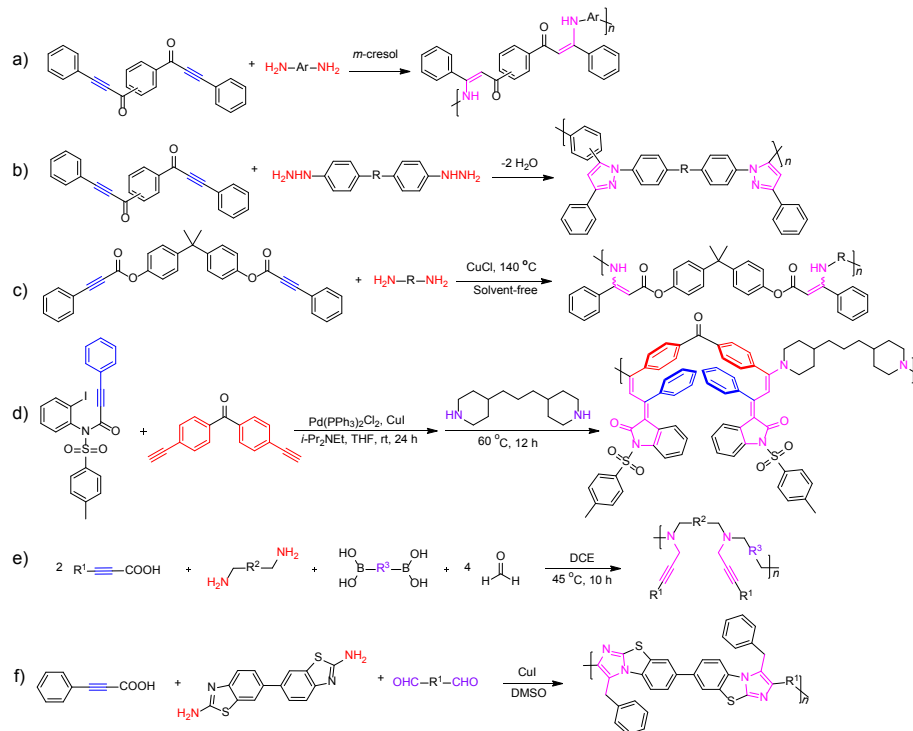
Scheme 3 Synthesis of poly(vinyl sulfide)s by thiol-yne polymerizations.



2.4. Amino-yne polymerization

Alongside the developments of azide-alkyne polycycloaddition and thiol-yne polymerization, advances were being made in the realm of amino-yne polymerization. As early as 1986, Bass and coworkers exploited the addition polymerization of a activated acetylenic ketones and aromatic diamines in *m*-cresol, furnishing thermally stable poly(enamine-ketone)s with superior mechanical and film-forming property in Z-isomeric configuration caused by the intramolecular hydrogen bond interaction (Scheme 4a).^[46]

Scheme 4 Synthesis of nitrogen-containing polymer by amino-yne polymerizations.



In the following year, they reported a cyclopolycondensation of aromatic dipropynones and hydrazines as a facile route to polypyrazoles with various molecular weights and thermal stabilities (Scheme 4b).^[47]

Not only carbonyl activating internal alkynes but also ester-activated ones can be utilized as monomers for polyhydroamination reaction. In 2016, Qin, Tang and coworkers reported an effective Cu(I)-catalyzed amino-yne click polymerization towards nitrogen-containing polymers (Scheme 4c).^[48] Under the catalysis of CuCl, the ester-activated internal alkynes and diamines could be polymerized in a regiospecific and stereoselective manner at 140 °C, and sole Markovnikov additive polyenamines with high Z-isomeric conformations (up to 94%) and high molecular weights (M_w up to 13500) could be readily synthesized in satisfied yields (up to 97%) after 2 h. Furthermore, the resultant polymers enjoyed high visible light transparency and strong UV-light shielding efficiency, making them applicable in advanced photonic areas. Taking advantage of its high efficiency, this amino-yne click polymerization has attracted researchers' attention from various fields, such as surface immobilization and modification, drug delivery, synthesis of hydrogel and macromolecular materials.^[49] It is worth noting that the polymerization described above were concerned with the incorporation of activated internal ethynyl moieties into the polymeric main chain. Actually, ethynyl units could also be used to decorate polymer backbone as the attached pendants. In 2019, Hu, Tang and coworkers utilized the multicomponent tandem polymerizations of propiolamide, aromatic terminal alkynes, and commercially available diamines, and a series of poly(indolone)s with complex structure, and high M_w (up to 30400) were generated in high yields (up to 97%). The unique chemical structures of poly(indolone)s enable them to be highly selective chemosensors toward trifluoromethanesulfonic acid detection in a fluorescence turn-on manner (Scheme 4d).^[50] Subsequently, they designed a carboxylic acid activated alkyne for an efficient catalyst-free four-component

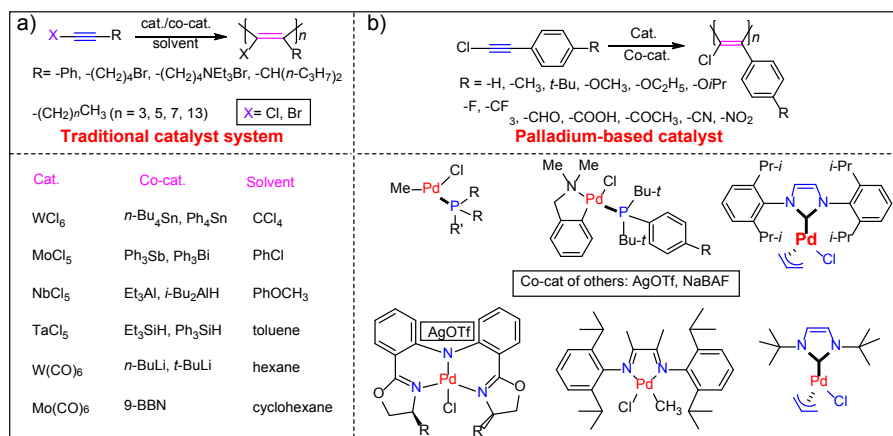
polymerization of propiolic acids, benzylamines, organoboronic acids, and formaldehyde (Scheme 4e). Thanks to the high reactivity of activated alkyne monomer, the polymerization propagated smoothly under mild condition at 45 °C in dichloroethane, affording soluble and thermally stable poly(propargylamine)s with high M_w (up to 13900) in high yields (up to 94%). The attractive refractive indices and low dispersion coefficient of the products might enable them to find applications in the field of optical display. Additionally, with TPE and tertiary amine moieties embedded in the polymer skeletons, these poly(propargylamine)s displayed unique AIE feature and citric acid-triggered fluorescence enhancement, which are applicable in luminescent materials.^[51]

During the surveying literatures on activated internal alkyne-based polymerization, we accidentally found that the acetylene acids could also be used to construct heterocyclic conjugated polymers. For example, in 2020, Cai, Zhang and coworkers reported a facile multicomponent polymerization of alkynedicarboxylic acid, heterocyclic diazole and dialdehydes, and fused heterocyclic polymers containing imidazo[2,1-b]thiazole units with relatively high M_n (up to 11000) were furnished in moderate yields (Scheme 4f). Bearing the special heterocycle section, the resultant polymers exhibited good solubility, salient optical activity, and low energy bands, demonstrating their potential application in photoelectric field.^[52]

2.5. Haloalkyne-based polymerization

Haloalkynes that have electron-withdrawing halogen substituents in conjugation with ethynyl groups are another type of attractive activated alkynes. This subsection intends to illustrate the versatility and potential of haloalkyne-based polymerization, which can be roughly summarized into three categories according to the type of halogen species. The first category is mainly based on chloroalkyne. As described above, PA is a archetypal conjugated polymer, and its chlorine substituted derivatives with better thermal and structural stability show potential applications in gas

Scheme 5 Synthesis of polyacetylenes by haloalkyne-based polymerizations.

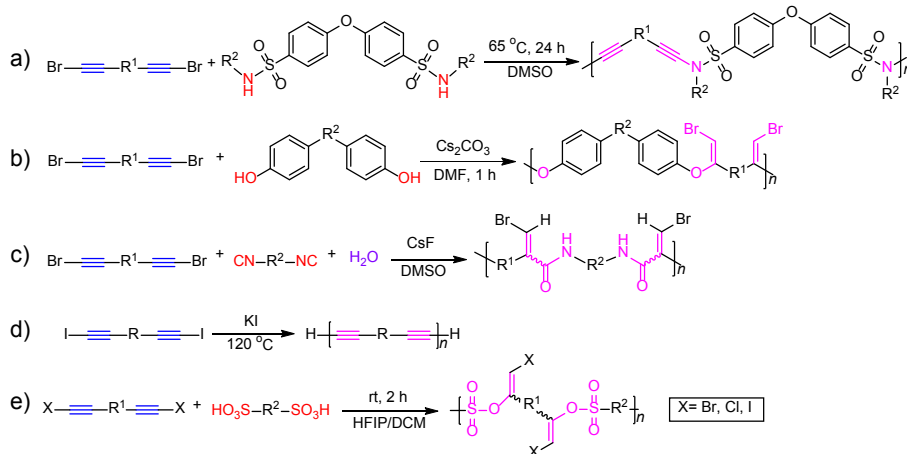


permission, electronic devices, fluorescence materials and so on.^[53-54] However, the polymerization of chlorine substituted acetylene monomers is difficult. Although classical transition metal catalysts of Mo, W, Nb, and Ta together with co-catalysts such as Ph₄Sn and Bu₄Sn have been explored. Nevertheless, their tolerance to moisture and polar groups is dissatisfactory in some cases, which limits their further development and practical applications distinctly (Scheme 5a).^[55-61] This situation changed in 2014, Sanda and coworkers reported that Pd-based complexes could catalyze the polymerization of acetylene monomers bearing polar groups.^[62] After this pioneering work, a series of studies concerning the polymerization of 1-chloro-2-phenylacetylene monomers by Pd-based catalytic systems were reported, and plentiful poly(1-chloro-2-phenylacetylene)s with various structures and diverse properties like lyotropic liquid crystallinity, chirality, and unique emission behaviors were yielded. On account of the appealing merits, these PAs are promising candidates for fluorescent sensors and probes to chemicals and external stimuli, as well as chiral transfer and circularly polarized luminescence materials (Scheme 5b).^[63-70]

The second category is chiefly concerned with bromoalkynes. One example is that alkynyl bromides and sulfonamides could be polymerized in the presence of CuSO₄·5H₂O, 1,10-phenanthroline, and K₂CO₃ at 65 °C in DMSO, generating poly(ynesulfonamides) with stable C_{sp}-N bonds and high *M_w* (up to 22000) in high yields

(up to 95%). Hu, Tang and coworkers adopted the numerous ethynynyl groups in the resultant polymers to react with Co₂(CO)₈ for the preparation of organometallics, which then underwent pyrolysis to fabricate magnetic ceramics with high magnetization and low coercivity (Scheme 6a).^[71] Furthermore, an efficient transition metal-free polymerization of bromoalkynes and phenols was developed by Qin, Tang and coworker. Soluble and thermally stable polymers with high *M_w* (up to 47600) were readily obtained in high yields (up to 95%) at 110 °C after 1 h. The AIE-active TPE-containing polymer could be used to fabricate a 2D fluorescent photopattern. The remaining bromovinyl groups in polymer backbone could further react with thiophenol derivative to endow the product with higher refractive index (Scheme 6b).^[72] Furthermore, Qin, Tang and coworkers developed an interesting polymerization of water and bromoalkynes and isocyanides, which propagated smoothly at 90 °C in DMSO in the presence of CsF, and functional polyamides with high *M_w* (up to 41700) and high fraction of *Z*-isomeric units (up to 80%) were generated in high yields (up to 98%). Thanks to their containing aromatic units, heteroatoms and bromoethylene groups as well as TPE motifs, the resulted polymers showed multiple functions, such as high refractive indices and aggregation-enhanced emission (AEE) characteristics. With abundant highly reactive bromoacrylamide groups in main chains, these polyamides could be post-modified through Sonogashira coupling and substitution reaction for further expansion of their functions (Scheme 6c).^[73]

Scheme 6 Synthetic illustration of haloalkyne-based polymerizations.



The third category is the iodoalkyne-based polymerization. In

2016, Lam, Tang and coworkers established an efficient KI-mediated homo-polycoupling of bis(iodoalkyne)s at 120 °C in DMF, generating three thermally stable polydiynes with high M_w (up to 20100) in satisfactory yields (up to 91%). By incorporating TPE units into the polymer main chain, a fluorescent pattern with high resolution could be generated readily. Moreover, some polymers possessed good solubility and could be fabricated into a tough thin films with super and UV-tunable refractive indices between 1.77 and 2.11 in a wide range of 400–900 wavelengths, indicative of a bright prospect for optical application (Scheme 6d).^[74]

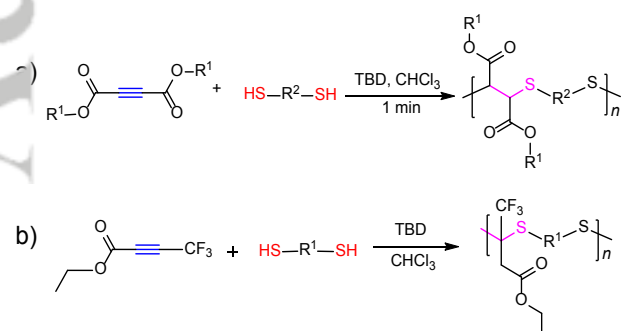
In addition, haloalkynes were also applied in the construction of functional polysulfonates. In 2021, Han, Lam, Tang and coworkers developed a catalyst-free spontaneous polymerization at room temperature in air with 100% atom economy for the in-situ preparation of photoresponsive polysulfonates with high M_w (up to 7900) in high yields (up to 94%). The halogen atoms embedded in the polymer skeleton not only rendered the polysulfonates with high and tunable refractive indices, but also enabled them to undergo post-functionalization for further function enrichment. Remarkably, the resulting polysulfonates could also show visible photodegradation and photoacid generation properties, offering them with wide application in various kinds of fields, such as photopatterning, and broad-spectrum antibacterial agents (Scheme 6e).^[75]

Polymerization of Di-Activated Internal Alkynes

3.1. Thiol-yne polymerization

When the triple bond is in neighboring connection with two electron-withdrawing groups, the di-activated internal alkynes will be very electron-deficient and active for nucleophilic addition and cycloaddition reactions. Durmaz and coworkers established an extremely fast polymerization of di-activated internal alkynes and thiols in the presence of an organobase of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).^[76–78] A series of polythioethers (PTEs) with high M_w (up to 47400) were obtained in high yields (up to 99%) just for 1 min. Furthermore, different activated alkynes were adopted to polymerize with 1,6-hexanedithiol, and the results demonstrated that dialkyl acetylenedicarboxylates (DAADs) were much more active than alkyl propiolates (M_w up to 8900, yield up to 91%) and methyl phenyl propiolates (M_w up to 1200). Moreover, the PTEs with thiols as the ending groups could react with *N*-phenyl maleimide in the presence of triethylamine at room temperature via thiol-ene click reaction with high post-modification ratio (up to 100%). Meanwhile, the ester groups at the side chain of PTEs could hydrolyze in the presence of an excess of trifluoroacetic acid (Scheme 7a).^[76] Later, Durmaz and coworkers used another

Scheme 7 Synthesis of sulfur-containing polymers by thiol-yne polymerizations.



commercially available di-activated alkyne monomer (*i.e.* 4,4,4-trifluoro-2-butyrate) to polymerize with various dithiols at room

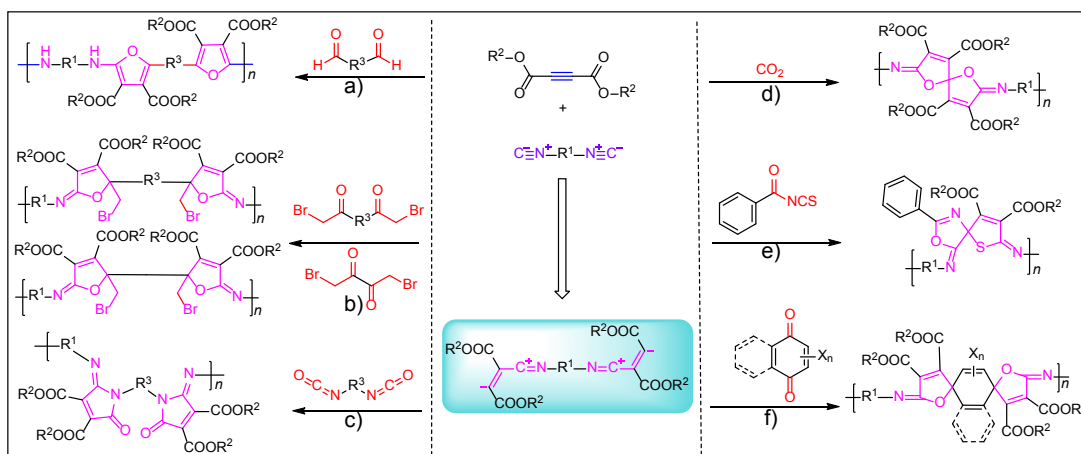
temperature in the presence of TBD (Scheme 7b).^[79] The polymerization performed very rapidly, and CF₃-substituted PTEs with high molecular weights (M_w up to 21100) were obtained after 1 min. Because of their contained lots of CF₃ groups, the polymers showed hydrophobic property with the contact angles ranging from 82 to 95°.

3.2. Isocyanide-based multicomponent polymerization (MCP)

MCP enjoys unique high efficiency, atom economy, simple reaction and isolation procedure, etc., is one of the most powerful synthetic methodologies for the rapid preparation of complex and multitudinous polymers. Isocyanide and alkyne are both promising monomers for the development of efficient MCPs because of their rich chemical property and potential unsaturated product structures. Active DAAD can be easily attacked by isocyanides to give zwitterionic intermediates, which are readily trapped by carbon electrophiles to generate polyheterocycles.^[80] Shi, Dong and coworkers developed a catalyst-free MCP of DAADs, diisocyanides and dialdehydes to afford fully substituted polyfurans with high M_w (up to 76400) in high yields (up to 91%). Surprisingly, one of polymers bearing dimethylbenzene moieties demonstrated the characteristics of black materials (Scheme 8a).^[81,82] The MCP mechanism probably goes through in following steps: isocyanide attacks the triple bond of DAAD to generate the zwitterionic intermediate; then, the electronegative olefinic carbon of the intermediate nucleophilically adds to the carbonyl carbon of the aldehyde group, meanwhile the oxygen atom of the carbonyl group attacks the positively charged carbon of the intermediate to produce the dihydrofuranone derivative, which subsequently experiences a [1,5]-hydrogen shift to generate furan unit. Shi, Dong and coworkers also established another MCP of DAADs, diisocyanides and bis(2-bromoacetyl)biphenyls or 1,4-dibromo-2,3-butanedione to construct polyiminofurans containing bromomethyl groups with high M_w (up to 24300) in high yields (up to 90%) (Scheme 8b).^[83–84] The polyfurans showed good degradability after UV light irradiation, which was attributed to the lots of UV-sensitive furan rings in the polymer main chains. Some of the polymers displayed AEE behaviors and could be good candidates for bioimaging and therapy of specific cells. Recently, Qin and coworkers explored a catalyst-free MCP of DAADs, diisocyanides and diisocyanates to prepare soluble and thermally stable poly(maleimide)s with high M_w (up to 29000) in satisfactory yields (up to 85%) (Scheme 8c).^[85] The resultant polymers displayed excellent film-forming ability, and their thin films possessed high refractive indices (up to 1.71 at 632.8 nm).

With the features of prominent mechanical, photoelectric oxidative, and thermal properties, heterocyclic spiropolymers are drawing increasing attention. Shi, Dong and coworkers prepared a kind of heterocyclic spiropolymers with 1,6-dioxospiro[4.4]nonane-3,8-diene as structural units, high M_w (up to 59000) in good yields (up to 88%) through the efficiently catalyst-free one-pot multicomponent spiropolymerization (MCSP) of DAADs, diisocyanides and green monomer of CO₂ (Scheme 8d).^[86] Cai, Dong, Kim and coworkers established another catalyst-free one-pot MCSP of DAADs, diisocyanides and benzoyl isothiocyanate toward spiropolymers containing 4,7-bis[alkyl(aryl)imino]-2-phenyl-3-oxa-6-thia-1-azaspiro[4.4]nona-1,8-diene moieties with high M_w (up to 34400) in good yields (up to 89%) (Scheme 8e).^[87] Particularly, part of the spiropolymers showed the unique clusterization-triggered emission property, and exhibited bright fluorescence in cancer cells by interacting strongly with the MDM2 protein, which could be used to distinguish cancer and normal cells. Notably, addition of spiropolymers to HepG2 cells facilitated a significant increase in intracellular reactive oxygen species to trigger apoptosis in cancer cells

Scheme 8 Synthesis of heterocyclic polymers by multicomponent polymerizations.



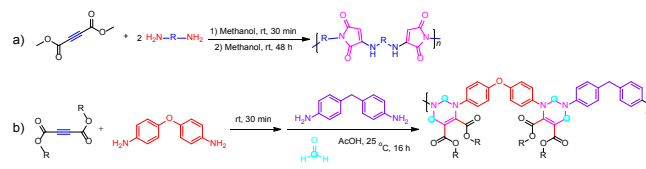
by releasing and activating the MDM2-bound p53, while displaying good biocompatible and non-toxic in normal cells. Recently, Shi, Long and coworkers explored a catalyst-free MCSP of DAADs, diisocyanides and halogenated quinones and prepared bis-spiropolymers with high M_w (up to 29200) in good yields (up to 88%) (Scheme 8f).^[88] It's worth noting that the bis-spiropolymers containing furan rings in the main chain showed obvious photodegradation with Rhodamine B as a visible light photosensitizer, indicative of great potential to be applied in pesticides.

3.3. Multicomponent tandem polymerization (MCTP)

With the compelling superiorities of MCPs and tandem polymerizations, it is attractive to combine them and develop efficient MCTPs for the preparation of macromolecules with advanced structures and unique properties. Toward this line, Lam, Tang and coworkers developed a catalyst-free MCTP of dimethyl acetylenedicarboxylate and amines (Scheme 9a).^[89] Poly(aminomaleimide)s with five-membered heterocycle and satisfactory M_w (up to 17800) were prepared in high yields (up to 99%). The polymerizations proceeded in two steps, including amino-yne click reaction and ring-closing reaction. When two different diamine monomers were used in each step, sequence-controlled polymers would be obtained. The resultant poly(aminomaleimide)s showed unusual nontraditional intrinsic luminescent (NTIL) properties, good biocompatibility and could act as a visualizing agent to target lysosome for cell imaging. To further enrich the variety of sequence-controlled polymers, Hu, Tang and coworkers established a metal-free MCTP of deactivated internal alkynes, aromatic diamines, and formaldehyde (Scheme 9b).^[90] By altering the order of monomer addition, poly(tetrahydropyrimidine)s with high M_w (up to 69800) were synthesized in high yields (up to 99%). Interestingly, the sequential regularity of tetrahydropyrimidines and dihydropyrrolones in the polymer backbone could be adjusted by controlling the reaction temperature and monomer loading ratio. All the polymers without typical luminophores in their structures showed NTIL properties. Moreover, multifunctional aromatic amines were employed to replace aromatic diamines in the MCTP to produce AIE-active hyperbranched poly(tetrahydropyrimidine)s with high M_w (up to 30000) in high yields (up to 98%).^[91] In addition, the flexibility of the MCTP has also allowed for the efficient formation of complicated π -conjugated poly(heterocycle)s with tunable properties.^[92-95]

Scheme 9 Synthesis of nitrogen-containing polymer by multicomponent

tandem polymerizations.

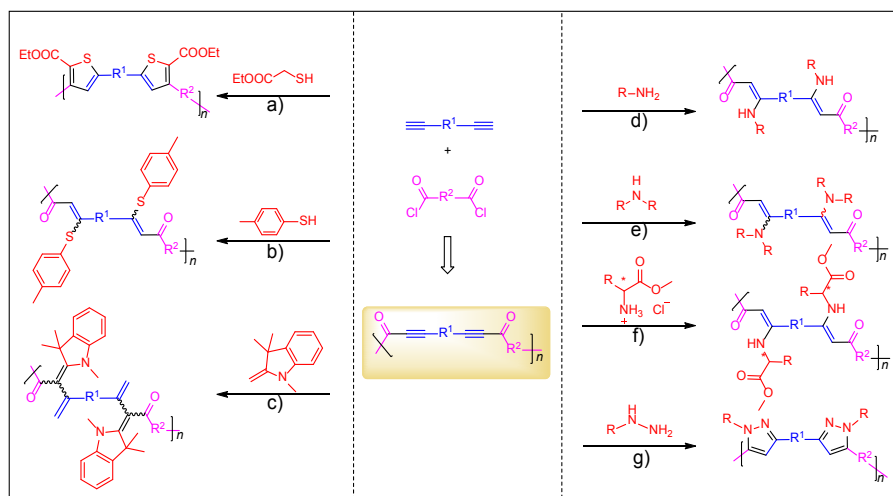


4. Polymerization of *in-situ* Generated Activated Internal Alkynes

To further maximize the structural diversity, reaction efficiency, and step-economy of polymerization methodology, the MCTPs of *in-situ* generated activated alkynes have been extensively studied toward diversely functional polymers. For example, Lam, Tang and coworkers developed a MCTP of alkyne, an acyl chloride, and ethyl 2-mercaptoacetate at room temperature (Scheme 10a).^[96] The MCTP mechanism probably performs in three steps: first, the Sonogashira coupling reaction between ethynyl groups and carbonyl chlorides to generate activated alkynes *in-situ*; secondly, the hydrothiolation reaction of electrophilic alkynone intermediates; finally, the cyclocondensation process to yield the thiophene rings with water as byproduct. The conjugated poly(arylene thiophene)s with high M_w (up to 156000) were readily prepared in high yields (up to 96%). Interestingly, the polymer thin film showed high refractive index, which could be further modulated by UV irradiation. The thiophene-containing conjugated polymer endowed with AEE behavior could be used to detect Ru(III) ion and to generate well-resolved fluorescent photopattern.

Next, the general applicability of MCTP to aliphatic and aromatic thiols was explored. Hu, Tang and coworkers developed a MCTP of alkyne, an acyl chloride, and aliphatic/aromatic thiols by combining the Sonogashira coupling and hydrothiolation processes (Scheme 10b).^[97] Different monomer strategies such as "A₂ + B₂ + C₁", "A₂ + B₁ + C₂", or "A₁ + B₂ + C₂" were employed to generate sulfur-rich conjugated polymers with tunable polymer backbones, high M_w (up to 59100), and high and controllable refractive indices in high yields (up to 98%). Later, the rapid access to the luminescent merocyanine-based polymers was reported by Hu, Tang and coworkers through a MCTP of alkyne, an acyl chloride, and Fischer's base (Scheme 10c).^[98] The conjugated poly(diene merocyanine)s were

Scheme 10 General illustration of in-situ generated activated internal alkyne-based polymerizations.



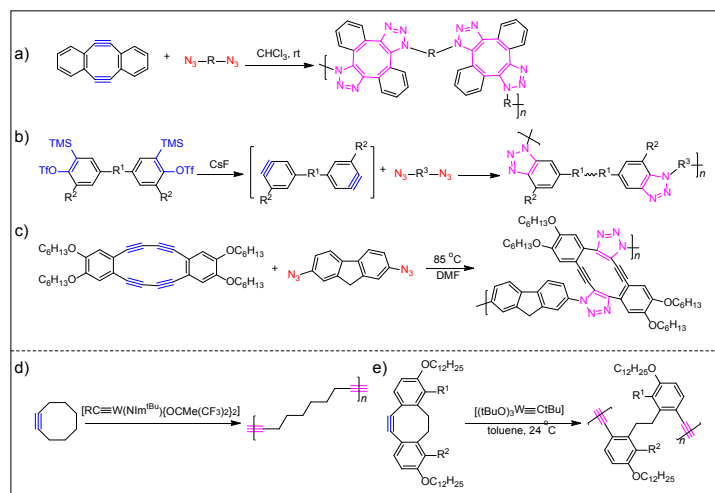
obtained with satisfactory M_w (up to 10900) in good yields (up to 81%). Afterwards, Lam, Tang and coworkers extended the concept of MCTP by using diynes, diaryl chlorides and primary amines to prepare nitrogen-containing conjugated polymers with high M_w (up to 46100), and high regio-/stereoregularities (*Z*-isomer up to 100%) in high yields (up to 99%) (Scheme 10d).^[99] Interestingly, when secondary amines were used in this MCTP, exclusively generating products with *E*-isomers of as high as 91% (Scheme 10e).^[100] The reason of high stereoregularity was that the products could form an intramolecular hydrogen bond between the hydrogen of -NH- and oxygen atom of carbonyl group. In addition, amino ester salts could also be used in this MCTP, and the resultant polymers inherited the chiroptical activities from the amine precursors (Scheme 10f).^[101] In addition, Hu, Tang and coworkers used hydrazines instead of amines to explore a MCTP with diynes and diaryl chlorides. Nitrogenous heterocyclic polypyrazoles with high M_w (up to 30700) were prepared in excellent yields (up to 97%) (Scheme 10g).^[102] With the compelling advantages of good processability, high light transparency and refractivity, and unique luminescence, it is foreseen that these polypyrazoles show potential in the

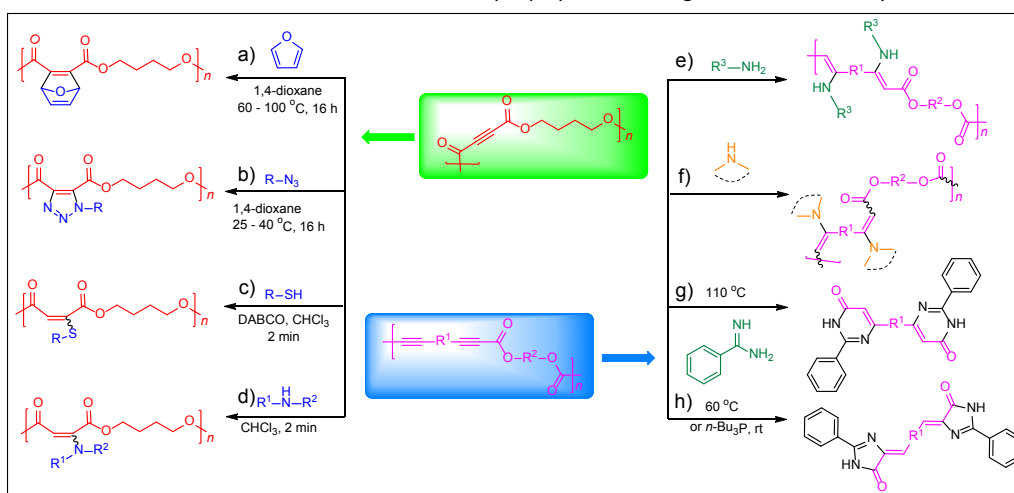
construction of conjugated semiconductors.

5. Polymerization of Ring-Strained Alkynes

Ring-strained alkynes are another viable activated alternatives besides the ones connecting with electron-withdrawing groups. In view of their high activity, they have been widely utilized in azide-alkyne polycycloaddition and ring-opening metathesis polymerization. In 2017, Zhang and coworkers developed a stoichiometric imbalance-promoted step polymerization using sym-dibenzo-1,5-cyclooctadiene-3,7-diyn and diazides as monomers without any catalyst or chemical stimulus (Scheme 11a). Polymers with varied isomer structures and high M_w (up to 407300) were prepared at ambient conditions. Meanwhile, in this kinetically controlled polymerization, cyclic oligomers could also be formed with a weight content above 30%.^[103] To enrich the family of ring-strained alkynes, Qin and coworkers designed benzyne monomers with highly strained six-membered carbon ring composing of two carbon-carbon double bond and one carbon-carbon triple bond,

Scheme 11 Schematic representation of ring-strained alkyne based polymerizations.



Scheme 12 Post-modification and functionality of polymers including activated internal alkynes.

and established a new benzyne-azide polycycloaddition (Scheme 11b). Di benzyne, which generated in-situ from their precursors in the presence of CsF, and diazides could be polymerized at 75 °C in acetonitrile/tetrahydrofuran, and soluble polybenzotriazoles with different regioregularities and high M_w (up to 13000) were produced in moderate yields (up to 75%) after 10 h. Combination of good light refractivity and AIE/AEE features, the generated benzotriazoles might potentially be useful in photic and biological fields.^[104] To develop the regioselective polycycloaddition of ring-strained alkyne and azide, Michinobu and coworkers synthesized octa-dehydridibenzo[12]annulene and applied it to polymerize with azides with the regiochemistry of the product being perfectly controlled (Scheme 11c). Heating the annulene and 2,7-diazidofluorene at 85 °C in DMF for two days furnished the PTA with M_w (up to 13800) in high yield (up to 79%).^[105] Taking advantage of the metal-free feature, this strain-promoted alkyne-azide polycycloaddition has been widely used in the synthesis of functional polymers for tissue engineering and therapeutic drug release.^[106-109]

Besides the ring-closing polymerization, the ring-opening one was also established. For example, Tamm and coworker and Nudelman and coworker independently exploited the tungsten- and molybdenum-based complexes coupling with diversified ligands to efficiently catalyze the ring-opening metathesis polymerization of strained cyclic alkynes, generating peculiar carbon materials with acetylene linkages along the polymeric backbone (Schemes 11d and 11e).^[110-114]

6. Post-Functionalization of Polymers Containing Activated Internal Alkynes

Post-modification of polymers is a compensatory technique to synthesize polymers with desirable functions and advanced structures owing to the absence of strategies to directly obtain from monomers. Durmaz and coworkers synthesized a kind of polyesters bearing di-activated internal alkynes in the main chains via esterification reaction of a cetylene dicarboxylic acids and diols as precursors for post-reaction. First, Diels-Alder cycloaddition reaction was used to modify the polyester with dienes compound at 60-100 °C for 16 h, and the graft ratio was up to 84% (Scheme 12a).^[115] Then, the efficient 1,3-dipolar cycloaddition reaction was adopted to modify the polyesters with azides at 25-40 °C, and the graft ratio was up to 100% (Scheme 12b).^[116] In addition, the oxanorbornadiene functional polymer was proven to undergo sequential 1,3-dipolar cycloaddition/retro-Diels-Alder reactions under mild conditions to release furan, and the total graft ratios varied between 75 to 79%. Moreover, thiol-yne and amino-yne click reactions were also used

to modify the polyesters (Schemes 12c and 12d).^[117] Under the catalysis of 1,4-diazabicyclo[2.2.2]octane, the efficiency of thiol-yne click reaction was 90% in 2 min, furnishing only mono-addition product with the E/Z ratio of 60/40. Whereas, when TBD was used, the double thiol addition products were gained with the graft ratios of up to 100%. Furthermore, when secondary amines were used to react with the polyesters without any catalyst, only *E*-isomers were obtained with 100% grafting ratio. While when primary amines were used as reactants, the graft ratio and fraction of *E*-isomers were up to 92% and 94%, respectively. In the context of green carbon scientific development for achieving "dual carbon" goal,

Qin, Tang and coworkers also contributed in this area. They established an efficient MCP of CO₂, diynes, and alkyl dihalides to yield polyesters bearing activated internal alkynes.^[118-120] Notably, when adding the fourth component of amines into the MCP, a four-component tandem polymerization was developed, and distinctly different stereoregularities of resultant poly(aminoacrylate)s were realized. Utilizing the primary amines produced polymers with 100% *Z*-isomers, whereas the secondary amines generated products with *E*-isomers up to 95% (Schemes 12e and 12f).^[121] By taking advantage of above MCTP, they also prepared multi-functional hyperbranched polymers and explored the applications in polyprodrug amphiphiles, white light-emitting devices and artificial light-harvesting system, etc.^[122] Moreover, Qin, Ling, Tang and coworkers also studied the degradation process of the CO₂-based linear and cross-linked unsaturated polyesters, which could be easily visualized by gradually increased luminescent intensity of the reaction mixtures.^[123] It is interesting to note that the polyesters were successfully degraded by benzamidine into diols and high-value-added pyrimidone at 110 °C, or imidazolone at 60 °C or in the presence of *n*-Bu₃P at room temperature (Schemes 12g and 12h). Moreover, the pyrimidone derivatives could be adopted in bioimaging and inhibiting bacteria, whereas the imidazolone derivatives could be used as a sensitive probe to detect Au(III) ion from electronic waste and *in-situ* generated bioamine from food spoilage.

7. Conclusions and Perspectives

In this review, we briefly summarize the recent advances in the polymerizations of mono-activated, di-activated acetylenes, in-situ generated and ring-strained alkynes. Meanwhile, the post-functionalization of polymers containing activated ethynyl groups were also reviewed. The functional polymers, as well as their versatile properties and diverse applications are also briefly described. Although remarkable progresses have been made in activated internal alkyne-based polymerizations, there remain numerous challenges

and vast opportunities in this area, providing the impetus for further research. First, the key for activated internal alkyne-based polymerizations to proceed lies in the expansion of new activated monomers and modes. Secondly, on a count of the endless pursuit of green carbon science, the step chasing highly efficient polymerizations of green monomer involved and catalyst-free systems should never be ceased. In addition, achievements in selective manipulation of product stereochemistry should be made to open new insight on structure-reactivity relationship, and to broaden the applications of polymer materials. Finally, as for these well-developed polymerizations and corresponding functional polymers with incomparable advantages, unremitting efforts are necessary for the development of their widespread applications in biological and optoelectronic fields. It is envisioned that future developments of fundamental researches and practical applications in activated internal alkyne-based polymer chemistry will ultimately bring benefits to the society.

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Activated Internal Alkyne-Based Polymerization

Baixue Li,[†] Jia Wang,[†] Benzhao He, Anjun Qin,^{*} and Ben Zhong Tang^{*}*Chin. J. Chem.* **2022**, *40*, XXX–XXX. DOI: 10.1002/cjoc.202200XXX

The recent progresses in the polymerization using activated internal alkynes, together with post-modification on pre-formed polymers containing a activated internal acetylene moieties were summarized. Through discussion of representative examples, it is hope to provide a powerful tool for the preparation of new polymers with well-defined structure, advanced functions, and versatile applications.