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Click Polymerization: Progresses, Challenges, and Opportunities

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ABSTRACT: Chemical transformations of small molecules have served as a rich source of reactions for the development of new polymerization processes, and "click" reaction has the potential to become a powerful polymerization technique. We herein give a brief account of the research efforts devoted to the development of click reaction into a new polymerization process. Remarkable progresses have been made in recent years in the exploration of metal-mediated and metal-free click polymerization systems and in the syntheses of linear and hyperbranched polytriazoles with regioregular molecular structures and advanced functional properties. We also discuss the existing limitations and challenges as well as the promising opportunities and directions in fostering the click polymerization into a versatile tool for the construction of new macromolecules with well-defined structures and multifaceted functionalities.

Introduction

Exploration of new polymerization reactions is a subject of enduring interest in the area of polymer research.[1] Most, if not all, polymerization processes have been developed from known organic reactions of small molecules. "Click reaction", coined by Sharpless et al. in 2001, is a chemical transformation with such advantageous characteristics as high efficiency, regioselectivity, and functionality tolerance as well as mild reaction conditions, fast reaction rates, and simple product isolation procedures.[2] The copper(I)-mediated cycloaddition of azide and alkyne reported independently by the research groups of Sharpless and Meldal in 2002 is an archetypical example of click reaction.[3] Click chemistry has found widespread applications in various research areas, for example, for the syntheses of bioconjugates and dendrimers and for the chemical modifications of surfaces and nanostructures.[4] It has also been utilized in macromolecule science, but the research activity has been mainly on the postfunctionalization of preformed polymers through polymer reactions.[5]

The azide−alkyne click reaction has great potential to become a powerful polymerization technique. Functional polymers have traditionally been mainly prepared by step-growth polymerization reactions such as condensation and coupling polymerizations. Polyesters and polyarylenes, for example, have commonly been synthesized by the condensation polymerizations of diacids and diols and the coupling polymerizations of arylboronic acids and aryl halides, respectively. These reactions, however, are often slow due to the sluggish reactivity of the monomers and have poor atom economy because of the formation of large amounts of small-molecule byproducts. Azide and alkyne, on the other hand, can be readily activated to generate highly reactive species, and their click polymerizations can theoretically be very fast and afford polymeric products with high molecular weights. The click polymerization should have excellent atom economy because the azide−alkyne reaction is additive (cycloaddition) in nature, while the orthogonality of the click reaction circumvents the problem of side-product formation and impurity contamination and enables the synthesis of polymers with high structural purity and molecular weights. Furthermore, the great functionality tolerance of the click polymerization makes it easy to incorporate electron-rich heteroatoms and polar groups into macromolecular architectures. The click polymerization is thus envisioned to be an efficient process for the synthesis of new functional polymers.

Attracted by the prospect, synthetic polymer chemists tried to utilize the azide−alkyne click reaction to prepare polytriazoles (PTAs) since 2004.[6,7] The early attempts, however, met with great difficulty and limited success, with slow reaction rates and low product solubility being the particular obstacles to the research efforts. Great progress has been made in recent years through such research endeavors as design of monomer structures, exploration of catalyst systems, and control of reaction conditions. In this Perspective, we will briefly summarize the advances in the area of research. Although there are still challenges to overcome, opportunities are plenty and the outlook is bright: the click polymerization will be nurtured into a powerful and versatile polymerization technique; during the course, new building blocks will be explored, new catalyst systems will be invented, new reaction routes will be established, and new functional polymers will be created.

The theme of this Perspective is on click polymerization. The research efforts directed toward the utilization of click reaction for preparation of dendrimers, postfunctionalization of preformed polymers, and generation of functional surfaces of polymer films will thus not be included in this paper because the topics have already been thoroughly discussed in several recently published excellent reviews.[4,5] Interested readers are referred to those review articles and cited references therein.

Progresses in Click Polymerization

Polymerization Processes. Typical click reactions of azides and alkynes are conducted in aqueous media and catalyzed by the copper(I) species in situ generated through the redox

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reaction of $CuSO_4$ with sodium ascorbate (SA).[3a] These "standard" click reaction conditions are appropriate for the preparations of dendritic oligomers, which were pioneered by Hawker and co-workers,[8] but not well suited for the syntheses of high molecular weight polymers. The incompatibility between the propagating species and the aqueous media induces the linear polymer chains or hyperbranched polymer spheres to agglomerate and eventually precipitate,[9] as evidenced by the experiment of Voit et al., which was the first attempt in the synthesis of PTAs employing the click reaction.[6] Voit and co-workers conducted the polymerization of 3,5-bis(propargyoxy)benzyl azide in the presence of $CuSO_4$/SA in a water/DMF mixture (1:2 by volume) but obtained a brown rubbery product that was not soluble in any organic solvents.

Soluble 1,4-regioregular PTAs, however, can be prepared by avoiding using water or minimizing the amount of water in the solvent mixture. Li and co-workers, for example, successfully prepared soluble hyperbranched PTAs from the click polymerization of an AB_2 monomer (Scheme 1) by decreasing the amount of water in the water/DMF mixture to 1:20 by volume.[10] Although Li's AB_2 monomers can be stored for about 1 month without suffering from any structural changes, such monomers are generally prepared by laborious experimental procedures and tend to undergo undesired self-oligomerization or autopolymerization during their preparation and storage due to the existence of two mutually reactive functional groups in a single molecular species.

The strategy of using an $A_2 + B_3$ monomer combination can solve the problem of self-oligomerization (Scheme 2), although there is a concern that such process may involve cross-linking reaction, leading to the formation of insoluble networks. Our and other groups have succeeded in the syntheses of soluble hyperbranched PTAs from the click polymerizations of diazide and triyne monomers by quenching the polymerization reactions before they reach the gel points.[9,11] When the $CuSO_4$/SA catalyst was used to catalyze the $A_2 + B_3$ click polymerization in the water/DMF mixtures with minimal water contents, 1,4-regioregular PTAs were obtained, but the polymers were only soluble in highly polar solvents such as DMF and DMSO.[9] Delightfully, when the diazide and triyne monomers were mixed in organic solvents in the presence of an organosoluble catalyst of $Cu(PPh_3)_3Br$, 1,4-regioregular hyperbranched PTAs were formed, which showed excellent solubility in common organic solvents, such as THF, chloroform, and dichloromethane.

Synthesis of 1,5-regioregular PTAs is of interest because the regiostructure may affect the polymer properties. While the copper(I)-catalyzed click reaction produces only 1,4-disubstituted 1,2,3-triazole derivative, ruthenium complexes such as $Cp^*Ru(PPh_3)_2Cl$ (Cp^* = 1,2,3,4,5-pentamethylcyclopentadiene) can efficiently catalyze azide−alkyne click reaction to yield exclusively 1,5-disubstituted 1,2,3-triazole derivative.[12] Employing this new catalysts system, we succeeded in synthesizing 1,5-regioregular PTAs with high molecular weights in high yields in short times under mild conditions (Scheme 2).[9] We found that $[Cp^*RuCl_2]_n$, the precursor of $Cp^*Ru(PPh_3)_2Cl$, was also effective in catalyzing the azide−alkyne click polymerization.

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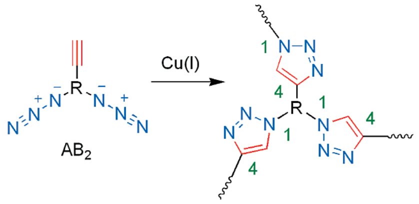
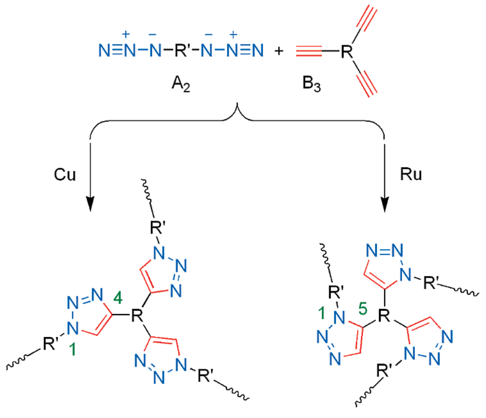
Jacky W. Y. Lam received his PhD degree from HKUST in 2003 under the supervision of Prof. Tang. In 2003−2007, he conducted postdoctoral research in Tang's group on conjugated polymers with linear and hyperbranched structures and advanced functional properties. He is currently a research assistant professor of chemistry at HKUST.

Ben Zhong Tang received his B.S. degree from South China University of Technology, China, and Ph.D. degree from Kyoto University, Japan. He did his postdoctoral work at University of Toronto, Canada. He joined HKUST in 1994 and was promoted to Chair Professor of Chemistry in 2008. He is interested in the creation of new polymers with novel structures and unique properties. He received a Natural Science Award from Chinese Government and a Senior Research Fellowship from Croucher Foundation in 2007 and was elected to Chinese Academy of Sciences in 2009. He serves as a science news contributor to *Noteworthy Chemistry* (ACS) and is a member of the editorial boards of a dozen journals, including *Progress in Polymer Science* (Elsevier), *Macromolecules* (ACS), and *Polymer Chemistry* (RSC).

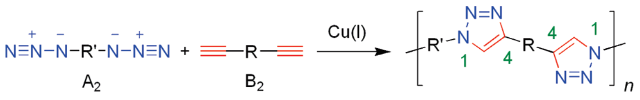
Scheme 1. Synthesis of 1,4-Regioregular Hyperbranched PTA by Copper(I)-Mediated Click Polymerization of Ethynylene Diazides (AB_2) Monomer



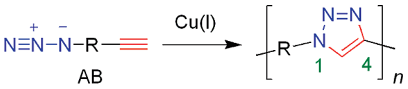
Scheme 2. Syntheses of 1,4- and 1,5-Regioregular Hyperbranched PTAs by Cu- and Ru-Catalyzed Click Polymerizations of Diazide (A_2) and Triyne (B_3) Monomers



Scheme 3. Synthesis of 1,4-Regioregular Linear PTA by Cu(I)-Catalyzed Click Polymerization of Diazide (A_2) and Diyne (B_2) Monomers

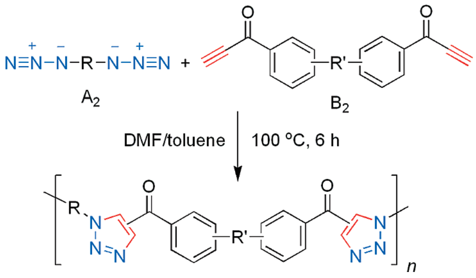


Scheme 4. Synthesis of 1,4-Regioregular Linear PTA by Cu(I)-Catalyzed Click Polymerization of Azidoacetylene (AB) Monomer

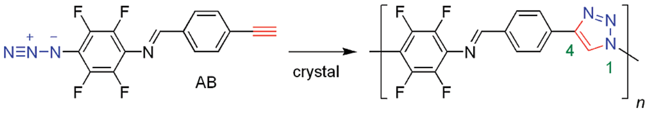


Many research groups have worked on the synthesis of linear PTAs by click polymerizations because such polymerizations are free of cross-linking problems. The copper(I)-catalyzed click polymerizations of diazide and dialkyne ($A_2 + B_2$; Scheme 3) or azidoacetylene (AB; Scheme 4) have been extensively investigated since the pioneering work of Matyjaszewski and co-workers in 2005.[13−19] Although the Cu(I)-catalyzed click reaction is fast for the syntheses of small molecules, it is sluggish for the polymer preparation, taking as long as up to 10 days for a polymerization reaction to complete. Furthermore, the obtained polymers are poorly soluble unless very long alkyl pendants or spacers are incorporated into the polymer structures.

Scheme 5. Synthesis of PATAs Rich in 1,4-Regiostructure by Metal-Free, Thermally Initiated, Click Polymerization of Diazide (A_2) and Bis(arolyacetylene) (B_2) Monomers



Scheme 6. Synthesis of 1,4-Regioregular PTA by Topopolymerization of Azidoacetylene in the Crystalline State



The PTAs obtained from the metal-catalyzed click polymerizations are difficult to purify because of the difficulty in complete removal of the catalyst residues from the polymeric products. The metallic residues are generally detrimental to electronic and optical properties of polymers. Light emissions of conjugated polymers, for example, can be quenched by the metallic traps. Furthermore, the transition-metal catalysts are expensive and cytotoxic, which become problematic when the polymerizations are conducted in biological systems or when the polymers are used for biological applications. Some of the organometallic catalysts are difficult to prepare, involving harsh reaction conditions and requiring nontrivial synthetic skills. Minimal use of metallic catalysts and development of metal-free polymerization systems are thus highly desired.

During the course of our study on the development of new polymerization reactions based on triple-bond building blocks, we have found that aroylacetylene and propiolate derivatives are more reactive than “normal” alkynes due to the electron-withdrawing effect of the carbonyl and ester groups adjacent to the carbon−carbon triple bonds and that the monomers can be polycyclotrimerized by nonmetallic catalyst systems.[20] We thus tried to use these reactive alkynes for the cycloaddition polymerization with azides. We succeeded in the polymerization of diazides and bis(aroylacetylene)s in polar solvents such as DMF/toluene mixtures at a moderate temperature of 100 °C for a short period of time and obtained poly(aroyltriazole)s (PATAs) in high yields with high regioregularity [molar fraction of 1,4-regioisomer ($F_{1,4}$) up to ~95%) and excellent solubility in common organic solvents (Scheme 5).[21] The metal-free polymerization can propagate smoothly in an open atmosphere without protection from air and moisture. Since this metal-free system has the key features of a click reaction, it can thus be regarded as metal-free click polymerization. This system broadens the types of alkyne monomers and simplifies the processes of click polymerizations. Moreover, it completely eliminates the effect of the metallic residues on the properties of the polymers, facilitating their applications in areas of optoelectronics, biomedicine, etc.

Other research groups have also reported metal-free azide−alkyne polycycloaddition systems.[22] A research team led by Pei and Ma, for example, has found that a fluorinated azidoacetylene can undergo topopolymerization in the crystalline state under ambient conditions in a regiospecific manner to furnish a 1,4-regioregular PTA, thanks to the unique arene−perfluoroarene interactions involved in the crystal lattice (Scheme 6). The polymerization, however, takes a long period of time (14 days) to complete, which is thus an atypical “click polymerization”, according to Sharpless' definition for a click reaction.[2]

Catalyst Systems. To make a polymerization process environmentally benign, atomically economic, and stereo- and

Table 1. Examples of Click Polymerizations[a]

no.	catalyst	monomer	solvent	*T* (°C)	*t* (h)	$F_{1,4}$ (%)	ref
1	$CuSO_4$/SA	$A_2 + B_3$	DMF/H_2O	rt	28	100	11
2	$CuSO_4$/SA	A_2B	DMF	rt	10	100	10
3	$CuSO_4$/SA	$A_2 + B_2$	THF	rt	240	100	18d
4	$CuSO_4$/SA/TEA	$A_2 + B_2$	THF	30−35	48	100	17b
5	$CuSO_4$/SA	AB	*t*-BuOH/H_2O	60	20	100	15b
6	$CuSO_4$/SA	$A_2 + B_2$	*t*-BuOH/H_2O	rt	48	100	15d
				80	10−12		18b
7	$CuSO_4$/SA	AB	DMF/H_2O	rt	24	100	15e
8	$CuSO_4$/SA	AB	THF/DMF/H_2O	25	96	100	17e
9	CuBr/bPy	$A_2 + B_2$	1,4-dioxane	30	8−96	100	15f
10	CuBr	$A_2 + B_2$	DMF	50	30	100	16b
				20	70		17c
				rt	89		13
11	CuI	$A_2 + B_2$	DMF/pyridine	rt	16	100	16c
12	$Cu(OAc)_2$/Cu/TBTA	$A_2 + B_2$	THF/CH_3CN	25	170	100	19
13	CuOAc	AB	DMF	80	0.5	100	15a
14	CuOAc/microwave	AB	DMF	100	0.5	100	17d
15	$Cu(PPh_3)_3Br$	$A_2 + B_3$	DMF or THF	60	1.33	100	9
16	$Cu(PPh_3)_3Br$	$A_2 + B_2$	THF	60	2.5−12	100	16a
17	$CuIP(OEt)_3$	AB	chloroform	60	24	100	15c
18	$Cu(CH_3CN)_4PF_6$/Cu/DMEDA	$A_2 + B_2$	CH_3CN	rt	72−336	100	14
19	$Cp^*Ru(PPh_3)_2Cl$	$A_2 + B_3$	THF	60	0.5	0	9
20	$[Cp^*RuCl_2]_n$	$A_2 + B_3$	THF	40	2	0	9
21	$PtCl_2$/PMDETA	$A_2 + B_2$	DMF	80	20	nd	13b
22	Δ (metal-free)	$A_2 + B_2$	DMF/toluene	100	6	88−95	21

[a] Abbreviations: SA = sodium ascorbate, TEA = triethylamine, bPy = bipyridine, TBTA = trisbenzyltriazoylamine, DMEDA = *N,N′*-dimethylethylenediamine, PMDETA = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine, Δ = heating, A = azido group, B = ethynyl group, DMF = *N,N*-dimethylformamide, THF = tetrahydrofuran, *T* = reaction temperature, rt = room temperature, *t* = reaction time, $F_{1,4}$ = molar fraction of 1,4-disubstituted 1,2,3-triazole repeat unit in PTA or PATA [$= A_{1,4}/(A_{1,4} + A_{1,5}) = 100 - F_{1,5}$, where A_i = integrated area of *i* peak in the ^{1}H NMR spectrum of the polymer], and nd = not determined.

regioselective, the catalyst plays a crucial role. Exploration of new catalytic systems is thus at the heart of macromolecular science, especially in the area of development of new polymerization techniques. Thanks to the research efforts of polymer chemists, several effective catalyst systems for click polymerizations have been developed. The most widely used catalyst system is the $CuSO_4$/SA mixture, but it often gives insoluble products (Table 1). In many occasions, the polymerization reactions take very long time to complete (up to 10 days; Table 1, no. 3). To circumvent the problems, other Cu(I) compounds were screened, from which $Cu(PPh_3)_3Br$ was identified to be a good catalyst. The copper complex is soluble in common organic solvents and can dramatically accelerate the reaction rates, with the polymerization reactions often finished in a few hours (e.g., Table 1, no. 16).[16a] Most importantly, it affords PTAs that are completely soluble and readily processable.

As discussed above, the Cu- and Ru-mediated azide−alkyne click polymerizations give 1,4- and 1,5-regioregular polymers, respectively. $Cp^*Ru(PPh_3)_2Cl$ is an excellent catalyst and produces soluble 1,5-regioregular PTAs in 75% yield in as short as 30 min (Table 1, no. 19).[9] The ruthenium(II) complex, however, is difficult to prepare, requiring painstaking synthetic efforts, and is also difficult to handle due to its sensitivity to air and moisture. Dichloro(pentamethylcyclopentadienyl)ruthenium(III) oligomer $[Cp^*RuCl_2]_n$ is the precursor to the $Cp^*Ru(PPh_3)_2Cl$ complex and is found to be capable of catalyzing click polymerizations to furnish processable 1,5-regioregular PTAs in high yields (~85%) under mild reaction conditions (Table 1, no. 20).[9] Notably, this Ru(III) complex can be readily prepared in a high yield by simply refluxing $RuCl_3 \cdot nH_2O$ and pentamethylcyclopentadiene in ethanol for a few hours. The complex is also air-stable and easy to handle. It is thus an outstanding catalyst for the 1,5-regioselective click polymerization.

Catalytic systems beyond Cu and Ru have also been explored. Matyjaszewski and co-workers have found that $PtCl_2$, $PdCl_2$, and $NiCl_2$ can catalyze click polymerization, with the Pt system exhibiting the highest catalytic activity (Table 1, no. 21), although its regiospecificity was not reported.[13a] We have established a metal-free click polymerization system, in which the polymerizations of aroylacetylenes and azides are initiated by simply heating the reaction mixtures to 100 °C in the absence of any metallic species (Table 1, no. 22).[21] PATAs with high regioregularity, good solubility, and ready processability are obtained in high yields (up to 96%) in 6 h.

Functional Properties. Accompanying the synthetic studies discussed above, a variety of PTAs have been generated, which exhibit unique chemical and physical properties. Triphenylamine-containing hyperbranched PTAs synthesized by the thermal polycycloadditions of $A_2 + B_3$ monomer mixtures, for example, show excellent performances as adhesives for metal, especially iron, plates, probably due to the high binding affinities of the triazole rings of the polymers as well as their peripheral azide and alkyne groups to the metal surfaces (Figure 1).[23] Tensile strengths of the PTA adhesive (**II**) prepared from the monomer mixture with a x/y ratio of 4:3 are impressively high at room temperature (up to ~30 MPa). The adhesion strengths remain to be high, even after the metal plates glued together by polymer **II** have been annealed at a high temperature of 250 °C for 2 h. In other words, PTA **II** is a strong adhesive for metallic plates with high thermal stability, which may find applications in such high-tech areas as defense industry and space exploration.

A conjugated PTA consisting of benzene and triazole repeat units shows novel ionochromism: its light emission is quenched by metal ions due to the metal-binding affinity of its triazole units.[24] Conjugated PTAs containing fluorene units serve as excellent matrix materials for quasi-solid-state dye-sensitized solar cells.[17b] The fluorene-containing PTAs are highly fluorescent when molecularly dissolved in good solvents but become nonemissive when aggregated in the solid state or fabricated into thin films, owing to the notorious

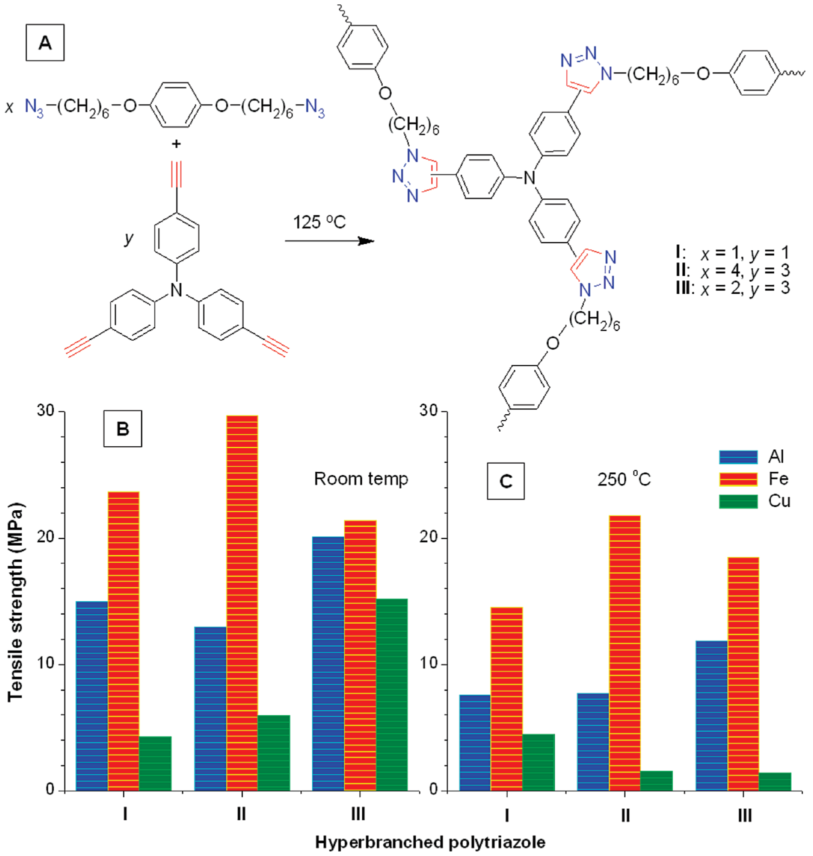


Figure 1. (A) Synthesis of hyperbranched PTAs (**I**–**III**) by heating the monomer mixtures with different compositions or diazide/triyne ratios (x/y) sandwiched between the plates of aluminum, iron, or copper at 125 °C. (B, C) Performances of the PTAs as thermally stable adhesives for metallic plates: tensile strengths of **I**–**III** (B) at room temperature and (C) after being annealed at 250 °C for 2 h.

effect of aggregation-caused emission quenching.[18d] An opposite phenomenon termed aggregation-induced emission (AIE), first discovered by our groups in 2001,[25] is observed in the tetraphenylethene (TPE)-containing PTAs and PATAs.[16a,21a] Although nonemissive in their solutions, the PATAs emit efficiently in the aggregate or solid state due to the AIE feature of the TPE units, as can be clearly seen from the examples of photographs shown in panels B and C of Figure 2.[26] Utilizing the novel AIE effect, the polymers are used as fluorescent chemosensors in either aggregate or film state for explosive detections with detection limit down to 0.1 ppm.

Thanks to the photoresponsive benzoyltriazole units in the PATAs, UV irradiation of their thin films through a photomask for 1 min causes the polymers to cross-link, directly generating fluorescent two-dimensional images without going through a development process (e.g., Figure 2D). Lengthening the irradiation time to 3 min, followed by the development of the photolyzed film with an appropriate solvent, furnishes a three-dimensional negative photopattern with a high resolution (Figure 2E). The readily polarizable aroyltriazole units in the PATAs endow the polymers with refractive indices (n up to 1.65) much higher than those of optical plastics or "organic glasses" such as poly(methyl methacrylate) (n = 1.49). The light refractivity of the PATA can be easily tuned to a large extent by a subtle structural change in its spacer length or R group (Figure 2).[21a]

Challenges and Opportunities

Although some impressive progress has been made (vide supra), the study of click polymerization is still a "young" area of research. To foster the click polymerization into a versatile synthetic tool is a task full of challenges yet rich in opportunities.

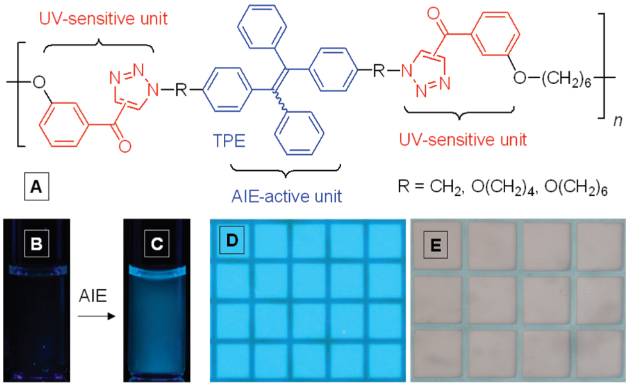
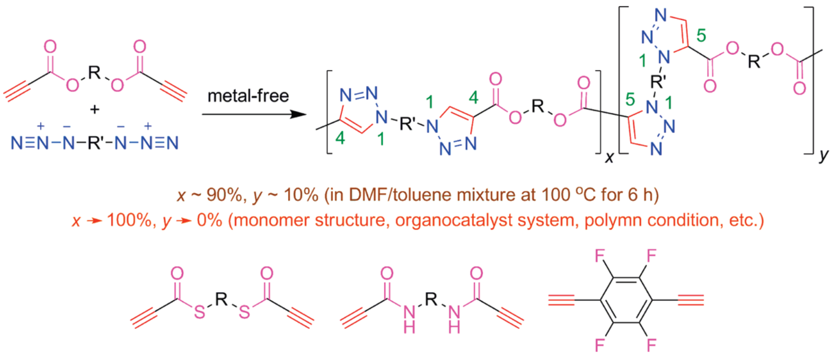


Figure 2. (A) Chemical structure of PATAs containing tetraphenylethene (TPE) repeat units. (B) THF solution of PATA (R = CH_2) and (C) its aggregates suspended in a THF/water (1:9) mixture. (D) Two-dimensional fluorescent image and (E) three-dimensional pattern generated by UV irradiation of the PATA for (D) 1 and (E) 3 min. Photographs were taken under (B–D) UV light illumination and (E) normal room lighting.

Catalyst Development. Since Sharpless and co-workers introduced the philosophical concept of click chemistry, many copper salts and organocopper complexes have been found to be capable of catalyzing azide–alkyne cycloaddition reaction efficiently and regioselectively. Whereas the catalysts are very effective for the preparations of small molecules, many of them, especially the "standard" click catalyst of $CuSO_4$/SA mixture, show rather low activity in the polymerization reactions for the syntheses of big polymers. The reactions are so sluggish that they often take

Scheme 7. Development of 1,4-Regioselective Metal-Free Click Polymerizations of Azide with Propiolate and Other Alkynes Containing Electron-Withdrawing Groups



days and sometimes even weeks to complete (cf. Table 1).[7a] Development of new copper(I) catalyst systems that can greatly speed up the cycloaddition polymerization reactions is thus an important proposition in the area of research, although it could be quite challenging.

The much faster rates of the click polymerization reactions initiated by the organosoluble catalyst of $Cu(PPh_3)_3Br$, in comparison to those of the reactions initiated by the $CuSO_4$/SA mixture,[9,16a] suggest that the poor solubility of the propagating species in the aqueous solutions of $CuSO_4$/SA is probably a key issue. The monomers take much time to find their pathways to reach the active species buried in the oligomeric or polymeric coils or spheres, thereby significantly slowing down the growth rates of the propagation reactions. An important target in the search for efficient catalyst systems is thus the copper complexes with high solubility in common organic solvents. It is hoped that the high efficiencies of the organocopper(I) catalysts may help minimize the amounts of the metallic species to be used in the click polymerization reactions.

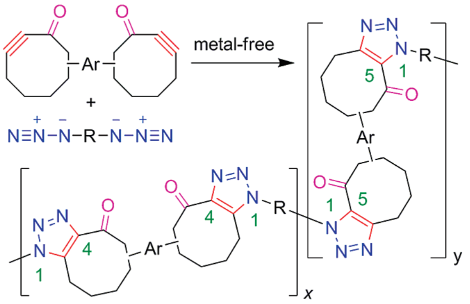
It has been well established that the organoruthenium complexes, such as $Cp^*Ru(PPh_3)_2Cl$, efficiently catalyze the click reactions of azides and terminal or internal alkynes in a 1,5-regiospecific manner.[12] Examples of utilizing the organoruthenium complexes to catalyze click polymerizations, however, has been rare,[9] although it provides a unique opportunity to study structure−property relationships of PTAs. Research on the Ru-mediated click polymerization is still in its infancy, mainly due to difficulty in the syntheses of the complexes, in addition to their environmental instability and limited variety. Although an example of ready-to-make and easy-to-use organoruthenium complex, i.e., $[Cp^*RuCl_2]_n$, has been identified,[9] much work remains to be done to explore the full potential of Ru complexes in the area of research on click polymerization. For example, search for new ligands with new coordination modes and development of simple synthetic routes may lead to the creation of new Ru complexes with well-balanced stability and reactivity (or catalytic activity). The metal center may also be changed from Ru to other transition metals that can coordinate with triple bonds, such as Rh, Ir, and Pt,[27] although these metals have seldom been used to mediate click reactions.[13b] Successes in these research endeavors may help push forward the area of study to a new height.

Recyclable and reusable solid matrix-supported metallic catalysts have been developed and used for preparations of low molar mass triazole derivatives.[12a,28] Application of such catalyst systems in the area of click polymerization will help simplify the isolation procedures of PTAs (e.g., by simple filtration) and minimize the detrimental effects of transition metals on their material properties, especially optical and photonic activities. The latter problem can alternatively be better solved or completely eliminated by using organocatalysts to initiate the click polymerizations. Since most biochemical reactions in the living systems are catalyzed by organic (e.g., enzymes), rather than metallic, species, the development of organocatalyst systems has become a hot subject of research in the area of synthetic organic chemistry. The information collected and the insights gained by the synthetic chemists may be borrowed to explore organocatalyst systems for click polymerizations. The regioselectivities of the thermally initiated metal-free click polymerizations reported by us are high but not yet perfect,[7a,21] and there is much room for improvement. It will be very exciting and rewarding if environmentally benign organocatalyst systems can be developed that can catalyze click polymerizations in high efficiency and perfect regioselectivity.

Structural Design. Design of proper monomer structures or exploration of new building blocks is another important theme in the area of polymer research. The establishment of the metal-free route for the click polymerization of azides and aroylacetylenes, though not yet perfect in terms of regiospecificity, is a remarkable progress in the area of research on click polymerization (cf. Scheme 5). This "green" process is worthy of further investigation. In addition to the search for new organocatalyst systems discussed above, the design of molecular structures of the monomers, such as tuning their electronic densities and attaching position-directing ancillaries to their skeletons, and the optimization of reaction conditions are among the strategies to be taken to make the polymerization process perfect and to push the regioselectivity to the desired limit (i.e., $F_{1,4} \rightarrow 100\%$).

Some examples of structural manipulations are shown in Scheme 7. Although the aroylacetylenes are excellent monomers in terms of orthogonal reactivity with azides (cf. Scheme 5), their syntheses are rather difficult and involve multistep chemical transformations.[20e] Propiolates are structurally similar to aroylacetylenes and can be facilely prepared from single-step esterifications of commercially available starting materials of propiolic acids and alcohols.[20b,29] Our experimental results indicate that, similar to aroylacetylenes, propiolates readily undergo thermally initiated metal-free click polymerizations: simply heating their mixtures with azides furnishes PTAs with $F_{1,4}$ values in the vicinity of 90% (Scheme 7). It is envisioned that when the oxygen atom in the propiolate is replaced by sulfur or nitrogen, the resultant prop-2-ynethioate and propiolamide may also be converted to PTAs by the metal-free polymerization process. The list of the monomers may be further expanded to include such electron-deficient alkynes as 1,4-diethynyl-2,3,5,6-tetrafluorobenzene. In these polymerization systems again the perfection of the reaction regiospecificity may be realized through

Scheme 8. Metal-Free Polycycloaddition of Azide and Strained Alkynes or Cyclooctyne Derivatives



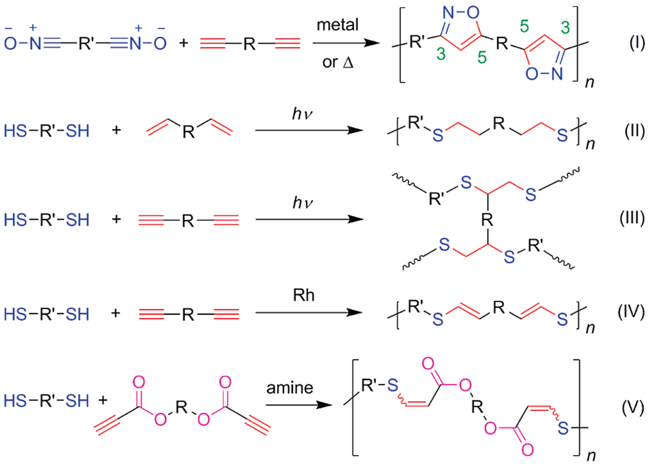
such endeavors as fine-tuning of monomer structures, development of organocatalyst systems, and optimization of polymerization processes.

Although the strain-promoted cycloaddition of azide and cyclooctyne is regiochemically nonspecific and thus may not be classified as a typical click reaction (as pointed out by a referee), it has found an array of applications in the area of biological research because it does not use poisoning Cu(I) catalyst and it is cytocompatible.[30] No polymers, however, have been prepared from this fast metal-free reaction, probably due to the synthetic difficulty in the preparations of cyclooctyne derivatives.[31] Exploration of simple synthetic routes to cyclooctyne derivatives will help cultivate this unique reaction into a useful metal-free polymerization technique. Integration of electron-withdrawing units such as carbonyl groups and fluorine atoms into the monomer structures may bestow the desired regioselectivity on the reaction, thereby making the polymerization readily "clickable" (Scheme 8).

The copper(I)-catalyzed azide–alkyne cycloaddition has been hailed as the "cream of the crop",[2,4] and the click polymerization processes developed so far have been mainly based on this click reaction.[7] Recent years have witnessed rapid progress in the development of other click reactions, examples of which include nitrile oxide–alkyne cycloaddition and thiol–ene and –yne hydrothiolations.[7] Research efforts, although rather scattered, have been devoted to expand the scope of click polymerizations through utilization of these new click reactions. For example, the click reactions of nitrile oxides (in situ generated from oximes) with alkynes have been employed to prepare 3,5-regioregular poly(isoxazole)s (Scheme 9I).[32] The photoinduced thiol–ene click reaction has been used to make cross-linked networks.[33] Similarly, the click polymerizations based on the thiol–yne click reaction activated by UV irradiation[34] yields sulfur-containing insoluble gels with hyperbranched structures that are macroscopically intractable (Scheme 9III).

We have recently succeeded in the syntheses of soluble poly(vinylene sulfide)s from thiol–yne click polymerizations.[33b] Instead of photoactivation, we used organorhodium complexes or secondary amines to catalyze the polymerization process, which can retain the reaction at the vinyl sulfide stage without further proceeding to alkyl sulfide. The Rh-catalyzed thiol–yne click polymerizations propagate in an anti-Markovnikov addition mode, affording stereoregular linear poly(vinylene sulfide)s with 100% *E*-conformation (Scheme 9IV). The click polymerizations of dithiols and dipropiolates can be mediated by nonmetallic catalysts of secondary amines, generating anti-Markovnikov products of linear polymers rich in *Z*-conformation (up to 81%). These processable poly(vinylene sulfide)s are of interest because sulfur-containing polymers often show unique functional properties, such as high and tunable refractive indexes.[33b]

Scheme 9. Expanding the Scope of Click Polymerization



Accompanying the expansion in the variety of click reactions, the territory of click polymerization is anticipated to be widened accordingly. The Michael addition of thiol and maleimide, for example, is a special type of thiol–ene reaction and may be utilized to develop new click polymerizations for the syntheses of heterocyclic polymers containing succinimide rings. Click polymerization based on Diels–Alder cycloaddition may enable the creation of functional polymers with reversible responses to stimuli, while Friedel–Crafts alkylation and acylation reactions may be employed to construct macromolecules from aromatic building blocks. With the growths in the number of new building blocks and the type of new polymerization processes, click polymerizations will be developed into a versatile synthetic tool for the creation of heteroatom-containing functional polymers that are difficult, if not impossible, to access by conventional polycondensation processes.

Functionality Exploration. The novel molecular structures of the click polymers are expected to give rise to unique functional properties, which warrant exploration. The triazole ring in the PTA, for example, is not just a structural linker to connect the monomer repeat units together but is multifaceted in functionality in its own right. The triazole ring is electron-deficient, and the PTAs thus may function as electron-transporting materials in the fabrication of organic light-emitting diodes. The triazole ring may also serve as electron-accepting unit to impart optical nonlinearity to the PTAs.[35] This is proved by our recent observation that hyperbranched PTA **I**′ ($F_{1,4}$ = 100%; x = 1, y = 1; cf. Figure 1A) exhibits remarkable nonlinear optical (NLO) activity because the polymer contains electron-donating (D) and -accepting (A) triphenylamine and triazole units, respectively (Figure 3). The push–pull interaction endows the polymer with large TPA cross sections (e.g., 470 GM at 720 nm). Its optical nonlinearity may become even larger at shorter wavelengths.

The nitrogen atoms in the triazole ring possess lone pairs of electrons, which are affinitive to cationic species and can coordinate with electron-deficient metallic ions through chelating interactions.[36] The PTAs comprised of the triazole repeat units can thus work as sensitive chemosensors to detect metal-based environmental pollutants and biological toxicants and as advanced adhesives to forcefully bind metallic structures and objects together.[23,24,37] The triazole unit is structurally similar to the amide bond of native peptide in terms of distance and planarity,[2,4] and its biocompatibility may allow the PTAs to find a wide variety of biomedical applications as, for example, polymer reagents in the preparation of bioconjugates, containers, or carriers

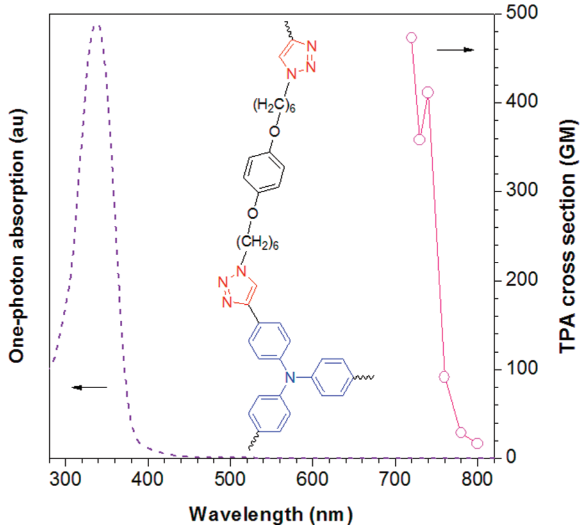


Figure 3. One- and two-photon absorption (TPA) spectra of hyperbranched PTA (**I**$^{\prime}$) containing donor and acceptor units.

for controlled drug delivery and cytophilic scaffold materials for tissue engineering.[17d]

The differences in the regiochemical conformations and stereochemical interactions between the 1,4- and 1,5-disubstituted 1,2,3-triazole units in the PTAs affect their topological structures and materials properties.[7a] The polymers with 1,4- and 1,5-regioregulary structures, for example, may take extended and compact conformations, respectively. Through chelating interactions with metals, a 1,5-regioregular PTA chain may behave like an unnatural foldamer to form a helical structure.[38] Because of the involved steric crowdedness, the 1,5-regioregular PTA is electronically less conjugated than its 1,4-counterpart, which has permitted color tuning of light emission from PTA by changing its regiostructure, as shown in our previous study.[9] Since effective conjugation length in a polymer affects not only its light emission but also many other electronic and optical properties, there are rich opportunities to seize along this line in the area of research.

In addition to the triazole rings in the backbone and skeleton of linear and hyperbranched PTAs, other functional groups can be incorporated into the polymer chains and spheres as “beads”, “pendants”, and “peripherals” to create new functionalities. For example, monomers containing electron-rich units other than the triphenylamine group discussed above can be polymerized to yield PTAs with various D−A combinations and orientations[39] with strengthened push−pull interactions and enhanced NLO activities. While PTAs are already rich in nitrogen, fusing other nitrogen-rich units (e.g., melamine) with PTAs will furnish polymers extremely rich in nitrogen, whose pyrolytic processes may produce carbon nitrides with great technological values. The sensitivities of PTAs as metal-ion chemosensors have been high, but their selectivities need to be improved. This may be achieved by integrating the ligand groups with binding affinities to specific metal ions into the macromolecular structures as pendant or peripheral units. Synthesis of PTAs containing biological receptors such as biotin and folate may generate bioprobes with high sensitivity and selectivity. Embedding biodegradable or enzyme-cleavable units in the PTA-based bioconjugates may lead to the creation of biomaterials that can undergo programmable decompositions under physiological conditions.[40]

Concluding Remarks

In this Perspective, we presented recent progresses and discussed existing challenges as well as new opportunities in the area of study on click polymerizations. Most of the click polymerizations, similar to the parent systems of click reactions,[3] have been mediated by Cu(I) catalysts, which produce PTAs with 1,4-regioregularity. The Ru-catalyzed click polymerizations, although much less investigated, furnish 1,5-regioregular PTAs. The metal-free click polymerizations of azides and electron-deficient alkynes readily proceed under mild conditions without excluding oxygen and moisture from the polymerization systems. The resultant PTAs are completely soluble in common organic solvents and can readily form thin solid films by a spin-coating process. The polymers exhibit unique functional properties, including ionochromism, thermoadhesion, photolithographic patterning, optical nonlinearity, aggregation-induced emission, and photovoltaic energy transformation.

Although exciting progress has been made, the area is just dawning, with many challenges yet rich opportunities waiting to be tackled and grasped. Future directions and endeavors in the area include development of new building blocks in addition to the azide and alkyne monomers, exploration of new click catalysts with high efficiency and regiospecificity, opening of new polymerization routes based on other click reactions, and control of polymerization processes via optimization of reaction conditions, among others. The enthusiastic efforts of polymer scientists will help realize the full potential of the click polymerizations over the conventional step-growth polymerizations. We are convinced that the area will be pushed forward at a rapid pace and that the click polymerization will soon be developed into a powerful and versatile tool for the syntheses of new polymers with well-defined molecular structures and advanced functional properties.

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