

Review

AZIDE-ALKYNE CLICK POLYMERIZATION: AN UPDATE*

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Abstract The great achievements of click chemistry have encouraged polymer scientists to use this reaction in their field. This review assembles an update of the advances of using azide-alkyne click polymerization to prepare functional polytriazoles (PTAs) with linear and hyperbranched structures. The Cu(I)-mediated click polymerization furnishes 1,4-regioregular PTAs, whereas, the metal-free click polymerization of propiolates and azides produces PTAs with 1,4-regioisomer contents up to 90%. The PTAs display advanced functions, such as aggregation-induced emission, thermal stability, biocompatibility and optical nonlinearity.

Keywords: Click polymerization; Azide; Alkyne; Polytriazole; Functionality.

INTRODUCTION

The last decade has witnessed the rapid growth of Cu(I)-catalyzed azide-alkyne cycloaddition, *i.e.* click chemistry^[1, 2]. Thanks to its remarkable features, such as mild reaction conditions, regioselectivity, high reaction rate, functionality tolerance and atom economy, click reaction has been widely used in synthesizing organic molecules, bioconjugates and dendrimers and in decorating surfaces of thin films and nanoparticles *etc*^[3–12]. Though most of works of applying the click reaction in polymer science have been focused on postfunctionalization of preformed polymers, the efforts are also paid in fostering this reaction into an efficient polymerization technique, *i.e.* click polymerization^[13–16].

Since the first attempt in 2004^[17], tremendous works have been done in using click polymerization to synthesize functional polytriazoles (PTAs), which have been summarized in our review and perspective papers recently^[18, 19]. Even in the past one year since our reviews, there are more than twenty reports on the use of click polymerization of azides and alkynes to synthesize functional PTAs with linear and hyperbranched structures. In this update, we will provide a brief summary of these papers. Similar to our previous reviews, the works about preparation of dendrimers and cross-linked polymers will not be included.

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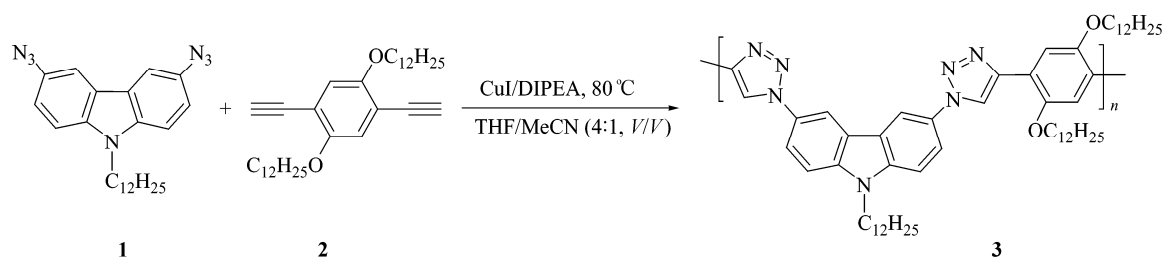
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PTAs WITH LINEAR STRUCTURES

Synthesis of Optically Active PTAs

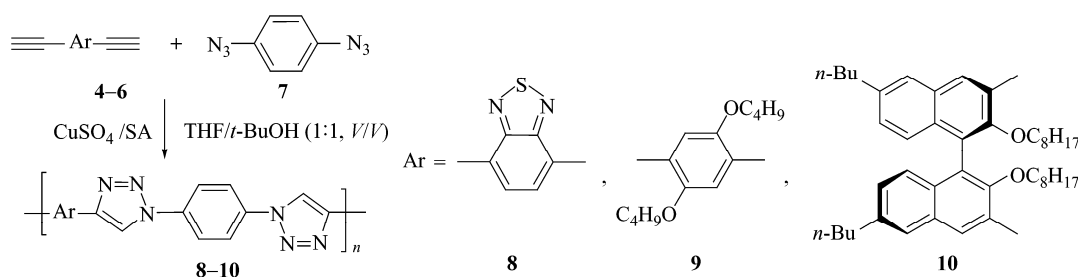
Conjugated polymers have found a variety of applications in optoelectronic devices, including light-emitting diodes, solar cells, field effect transistors and fluorescence sensors *etc*^[20–22]. The first example of conjugated polytriazoles was reported by Reek and coworkers in 2005^[23]. Since the triazole rings can act as conjugated units in polymers and as potential transition metal chelating sites, incorporating them into the polymer backbones is envisioned to generate new kind of materials with advanced functional properties.

Bielawski and coworkers synthesized the carbazole-containing main-chain PTAs by Cu(I)-catalyzed click polymerizations of 3,6-diazidocarbazoles and dialkynylarenes^[24]. The polymerizations were performed in degassed THF/MeCN solution (4:1, *V/V*) in the presence of CuI and 1,8-diazabicycloundec-7-ene (DBU) at 50°C for one week (Scheme 1). During the course, the reaction vessel was wrapped by aluminum foil to prevent the photolysis of CuI. Under the optimized reaction conditions [catalyst: CuI (2%)/*N,N*-diisopropylethylamine (12%), reaction temperature: 80°C], **1** and **2** were clickly polymerized to produce soluble polymer **3** with a high molecular weight in THF/MeCN mixture (4:1, *V/V*). The polymerization data indicate that the catalyst and reaction temperature significantly affect the molecular weights of the resultant polymers. The carbazole-containing PTA **3** is soluble and thermally stable ($T_d = 270^\circ\text{C}$). It emits blue light with maximum peak at 448 nm and photoluminescence quantum efficiency (Φ_F) of 0.29 in chloroform, which can make it potential in light-emitting diodes or other devices with blue emission.



Scheme 1 Synthesis of carbazole-containing conjugated PTA **3** by Cu(I)-catalyzed click polymerizations of diazide **1** and diyne **2**
DIPEA = *N,N*-diisopropylethylamine

Cheng and coworkers prepared conjugated PTAs as fluorescence sensors for metal ions^[25–27]. The click polymerizations of 4,7-diethynylbenzo[2,1,3]thiadiazole (**4**), 1,4-dibutoxy-2,5-diethynylbenzene (**5**) and (R)-6,6'-dibutyl-3,3'-diethynyl-2,2'-bisoctoxy-1,1'-binaphthyl (**6**) with 1,4-diazidobenzene (**7**) are carried out in THF/*t*-BuOH (1:1, *V/V*) mixtures in the presence of a catalytic amount of sodium ascorbate (SA) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Scheme 2). The produced polymers show moderate solubility in common organic solvents, such as toluene, THF, CHCl_3 and CH_2Cl_2 .



Scheme 2 Synthesis of PTAs by Cu(I)-catalyzed click polymerizations of diynes **4–6** and diazide **7**
SA = sodium ascorbate

The responsive optical properties of the conjugated PTAs on various metal ions have been investigated by photoluminescence (PL) and UV-Vis spectra. The results indicate that PTAs **8** show excellent fluorescence response for Ni^{2+} without interference from other metal ions (Fig. 1), whereas **9** and **10** can be used as selective fluorescence sensors for Hg^{2+} .

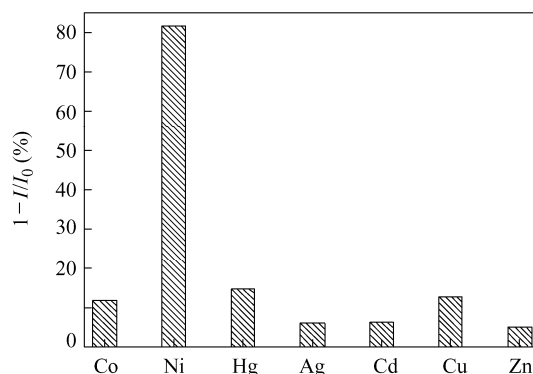
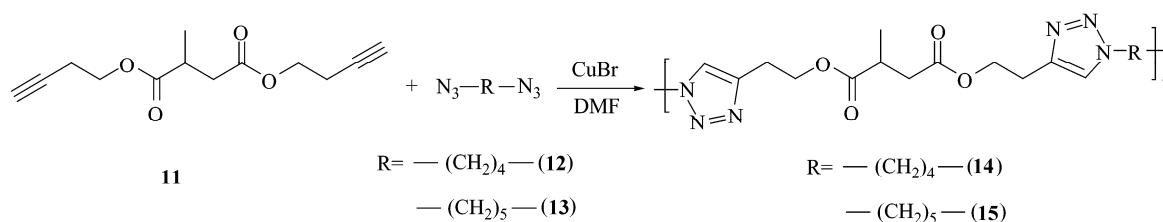


Fig. 1 Fluorescence quenching ratios of PTA **8** (10 $\mu\text{mol/L}$ in CHCl_3) in the presence of various metal ions (10 $\mu\text{mol/L}$) (Reproduced with permission from ref. [25]. Copyright 2009, Thieme)

Synthesis of Thermally Stable PTAs

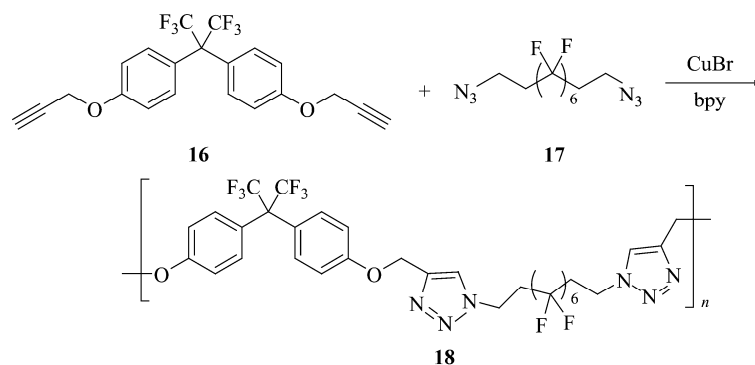
The polymers incorporating thermally stable triazole moieties are expected to show high resistance to thermolysis. Nagao and Takasu prepared thermally stable polyesters by CuBr-mediated click polymerizations of diynes containing ester linkages and diazides (Scheme 3)^[28]. The reactions are carried out in DMF at 50°C for 30 h, furnishing triazole-containing polyesters with high molecular weights (M_n up to 70000) in excellent yield (up to 99%). The polyester **14** synthesized from bis(butynyl)-methylsuccinate **11** and 1,4-diazidobutane **12** displays higher glass transition temperature ($T_g = 14^\circ\text{C}$) and melting temperature ($T_m = 125^\circ\text{C}$) than that of poly(octamethylene methylsuccinate) ($T_g = -53^\circ\text{C}$, T_m was not observed), which has no main-chain triazole rings. In contrast, the polyester **15** synthesized from 1,5-diazidopentane has much lower T_g (-4°C) and T_m (52°C), but its thermal properties are still superior to that of poly(octamethylene methylsuccinate). The results show that the thermal properties of the polyesters are improved in the presence of the main-chain triazole and could be controlled by changing the positions of the triazole rings.



Scheme 3 Synthesis of polyesters **14** and **15** by CuBr-mediated click polymerizations of diyne **11** with diazides **12** and **13**

Thanks to their highly thermal stabilities, chemical inertness and superior electrical insulating ability, fluoropolymers are attractive in development of advanced materials for high-tech applications, such as thin film coating, membranes for fuel cells and separators for lithium ion batteries^[29]. Ameduri and coworkers prepared original fluorinated copolymers containing triazole by CuBr-mediated click polymerization between telechelic aryl diynes and fluorinated telechelic diazides^[30]. Scheme 4 presents the synthetic route to PTA **18** from α,ω -dipropargyl ether hexafluorobisphenol AF (**16**) and telechelic fluorinated diazide (**17**) as an example. The

click polymerization was carried out in THF at room temperature using CuBr as the catalyst and 2,2'-bipyridine (bpy) as the ligand. The obtained fluorinated PTA exhibits interesting thermal and thermooxidative stability in the presence of the triazole rings, which can withstand high thermal temperatures (up to 550°C) under air.



Scheme 4 Synthesis of fluorinated PTA **18** via Cu(I)-catalyzed click polymerization of diyne **16** and diazide **17**
bpy = 2,2'-bipyridine

Other researchers have actively involved in the preparation of thermally stable PTAs by click polymerization^[31–34]. For examples, Huang and coworkers synthesized various arylacetylene terminated triazoleimide oligomers, which could be further cross-linked by Cu(I)-catalyzed click polymerization of diazides and imide-containing dialkyne in *N*-methyl-2-pyrrolidinone at 60°C under an open atmosphere^[31]. The resulting oligomers are soluble in organic polar solvents, and they were characterized by IR and ¹H-NMR spectra but their molecular weights were unknown. The *T_g* values and the decomposition temperature with 5% loss of their weights of the cured oligomers were measured to be 225–235°C and 385–393°C by differential scanning calorimetry and thermogravimetric analysis, respectively.

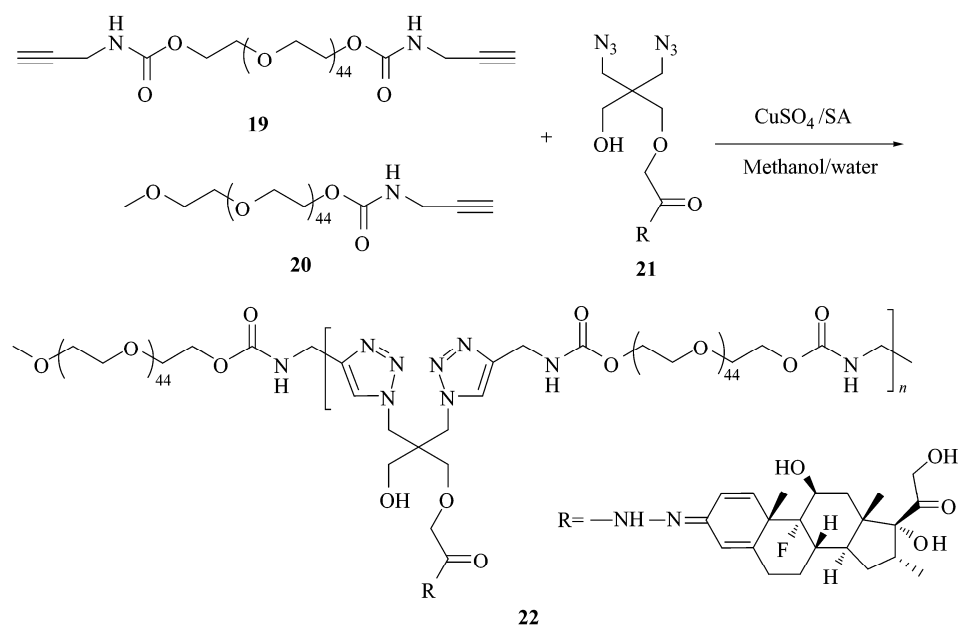
Chang and coworker prepared PTA/clay nanocomposites through in situ CuI-mediated click polymerization of α,ω -dipropargyl ether bisphenol A and 4-bis(azidomethyl)benzene in the presence of propargyl-functionalized clays^[32]. The PTA/clay nanocomposites dramatically improved thermal and mechanical properties compared to the pristine PTA.

Synthesis of Biocompatible PTAs

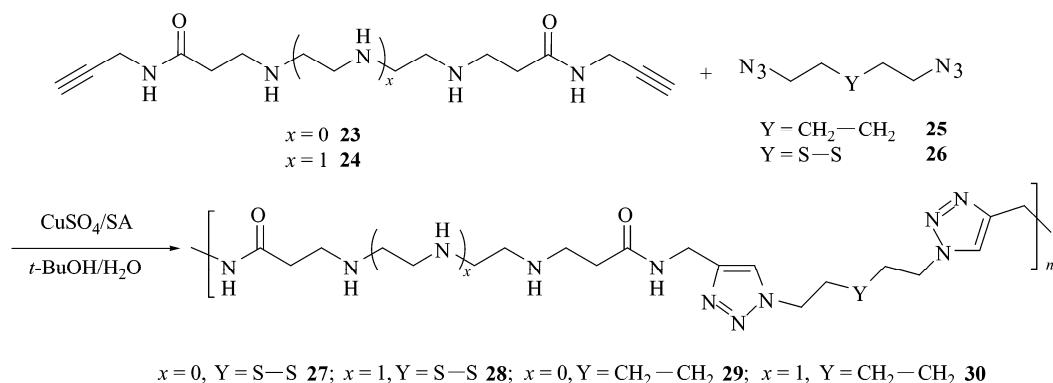
Thanks to the biocompatibility of triazole moieties, the click polymerization has also been utilized in efficiently synthesizing biomedical materials. Recently, Wang and coworkers prepared a multifunctional dexamethasone (Dex) containing polyethylene glycol (PEG) conjugate by Cu(I)-catalyzed click polymerization^[35]. As shown in Scheme 5, the PTA **22** was synthesized by the reaction of a PEG-containing diyne (**19**), mononye (**20**) and Dex-containing diazide (**21**) under an argon atmosphere in the presence of CuSO₄·5H₂O/sodium ascorbate and tris(hydroxylpropyl)triazolylmethylamine in methanol and water mixture. The acid-labile hydrazone bonds that connect Dex to PTA main-chains allow the drug to release in a pathophysiological environment and lead to sustained amelioration of joint inflammation in the adjuvant-induced arthritis rats tested. Compared to the more established polymeric drug delivery systems, PTA **22** has distinct advantages in synthesis, structural design and multifunctional loading capacity.

Cationic polymers as gene carriers have attracted much interest due to their advantages of non- or lower immunogenicity, tunable structures and ease of large scale production, *etc.* Du, Li and coworkers successfully synthesized a class of reduction-degradable cationic polymers with different secondary amine densities by Cu(I)-catalyzed click polymerization^[36]. The dialkyne-oligoamines (**23** and **24**) and diazides (**25** and **26**) are subjected to the polymerization at 60°C in *t*-BuOH/H₂O (1:1, *V/V*) mixture in the presence of CuSO₄/SA for 72 h (Scheme 6). The obtained polymers can bind and condense *p*DNA to form polyplexes. The PTAs **27** and **28**

containing the disulfide bonds condense DNA to form reduction-sensitive polyplexes that can be disrupted by dithiothreitol, exhibiting much lower cytotoxicity than their nonreducible counterparts **29** and **30**. The PTA **27** shows high transfection efficacy in the absence of serum, making it a good carrier for *in vitro* gene delivery by combining its low cytotoxicity.

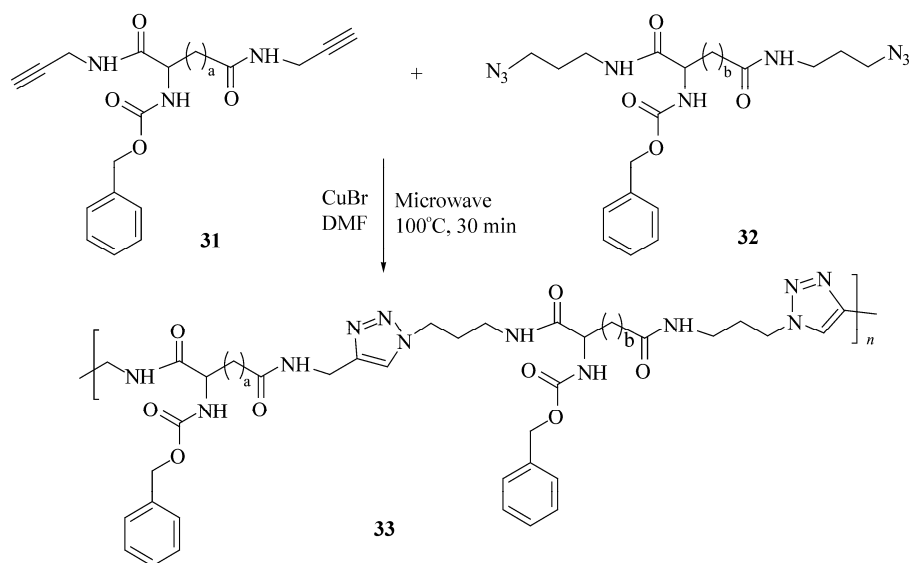


Scheme 5 Synthesis of click PEG-Dex **22** by Cu(I)-catalyzed click polymerizations
SA = sodium ascorbate



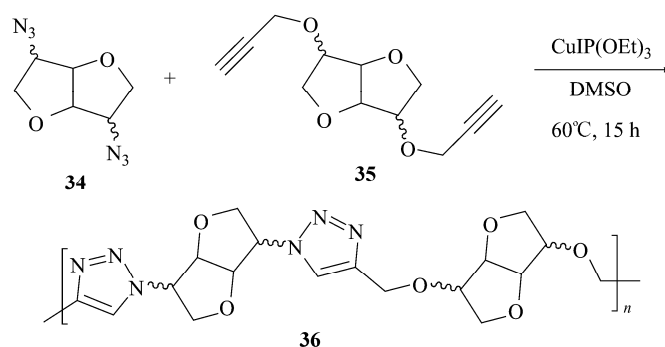
Scheme 6 Synthesis of cationic PTAs by Cu(I)-catalyzed click polymerizations of dialkyne **23** and **24** with diazides **25** and **26**
SA = sodium ascorbate

Huang and coworkers recently synthesized poly(ϵ -lysine) (ϵ -PL)-analogous polypeptides (**33**) through microwave-assisted Cu(I)-catalyzed click polymerization from aspartic (or glutamic) acid-based diyne (**31**) and diazide (**32**) monomers in 30 min (Scheme 7)^[37]. The deprotected polypeptides have relatively low cytotoxicity as ϵ -PL and could be used as substitutes of ϵ -PL in biomedical applications. The microwave-assisted click polymerization could pave a convenient way to synthesize ϵ -PL-analogous polymers and new series of the cationic polymers.



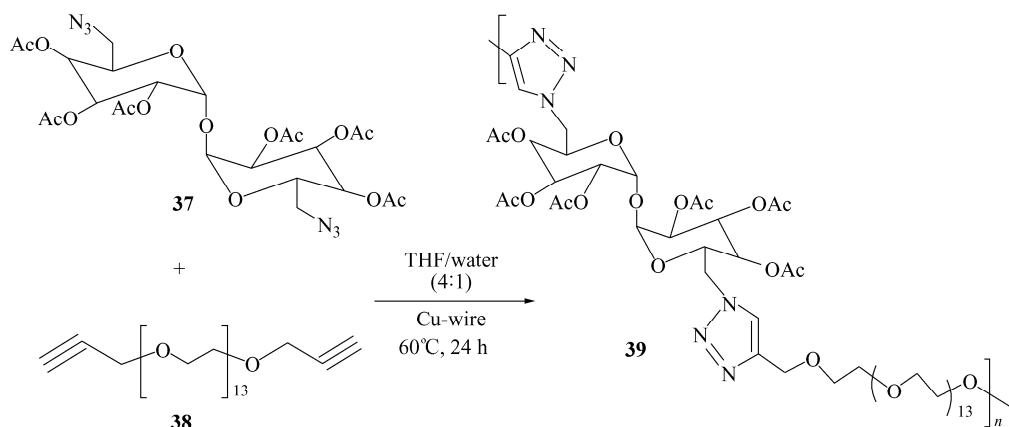
Scheme 7 Synthetic route to polypeptides **33** by microwave-assisted Cu(I)-catalyzed click polymerization

Drockenmuller, Bernard and coworkers have prepared a new family of starch-based PTAs with defined stereochemistry by CuIP(OEt)₃-mediated click polymerization of dialkyne and diazide functionalized dianhydrohexitol stereoisomers^[38]. Scheme 8 shows the synthetic route to PTA **36** as an example. This method could produce PTAs with high biosourced weight fractions (superior to 60 wt%) and high molecular weights (M_n up to 17000). The obtained PTAs are amorphous and have high glass transition temperatures ($T_g = 125\text{--}166^\circ\text{C}$) as well as good resistance to thermal degradation (the temperatures of 10% of their weight loss are $325\text{--}347^\circ\text{C}$).



Scheme 8 Synthesis of PTA **36** by Cu(I)-catalyzed click polymerization

Eissa and Khosravi synthesized a water-soluble and thermo-responsive glycopolymers *via* copper wire-catalyzed click polymerization of PEG-containing diyne (**37**) and trehalose-containing diazide (**38**) (Scheme 9)^[39]. The reaction was carried out in THF/water (4:1, *V/V*) mixture at 60°C using Cu-wire as the catalyst for 24 h. The obtained glycopolymers **39** shows a lower critical solution temperature within physiological range of about 39°C , which is well-known as fever temperature of human being. Due to the contained PEG and trehalose moieties, PTA **39** is anticipated to be biocompatible and biodegradable.

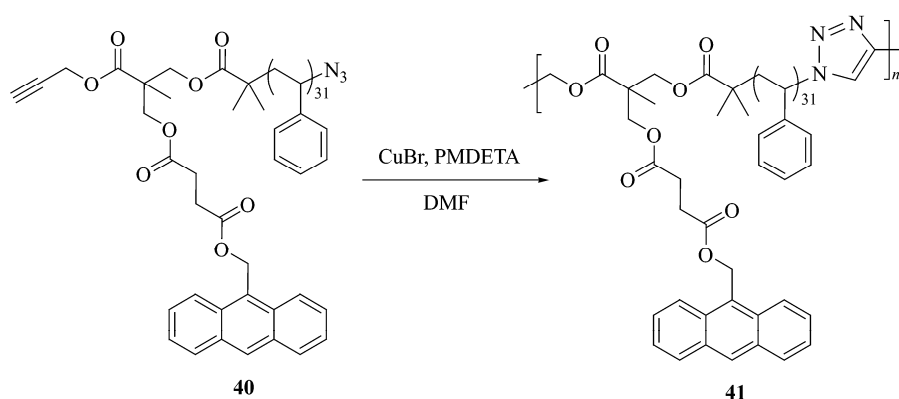


Scheme 9 Synthesis of thermo-responsive glycopolymer **39** by Cu wire-catalyzed click polymerization of diazide **37** and diyne **38**

Synthesis of PTAs from Macromonomers

The α -alkyne- ω -azide polymer chains are usually used to synthesize macrocyclic polymers. Such macromonomers can also be applied to prepare linear PTAs with relatively higher monomer concentration^[40, 41]. More recently, Tunca and coworkers successfully prepared linear and well-defined multiblock polystyrene (PS) with anthracene pendant site per PS block *via* CuBr-catalyzed azide-alkyne click polymerization (Scheme 10)^[42].

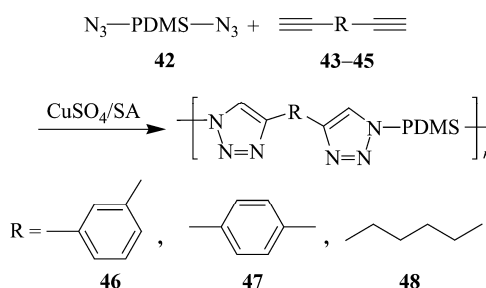
Macromonomer **40** with M_n of 3600 was prepared *via* atom transfer radical polymerization (ATRP) of styrene initiated by anthracene-containing compound in the presence of CuBr and PMDETA, followed by azide substitution reaction. The click polymerization of **40** was carried out in DMF at room temperature for 48 h, producing multiblock copolymer **41** with high molecular weight ($M_n = 42400$). Thanks to the contained anthracene units, the PTA **41** can further undergo the Diels-Alder click polymerization with maleimide end-functionalized poly(methyl methacrylate) (PMMA), poly(*tert*-butyl acrylate) (PtBA) or PEG, yielding PS-*g*-PMMA, PS-*g*-PtBA or PS-*g*-PEG copolymers with regular grafts, respectively.



Scheme 10 Synthesis of regular graft PTAs **41** by Cu(I)-catalyzed click polymerization of macromonomer **40**
PMDETA = *N,N,N',N'',N'''*-pentamethyldiethylenetriamine

Rieger and coworkers synthesized poly(siloxane) block polymer with high molecular weights from the macromonomer of α,ω -diazidooligo(dimethylsiloxane) **42** (N_3 -PDMS- N_3 , degree of polymerization around 5) and organic dialkynes *via* Cu(I)-catalyzed click polymerizations in THF/water or *t*-BuOH/water mixtures (Scheme 11)^[43]. Though the PTAs possess comparable molecular weights, **46** and **47** are elastic solids, whereas,

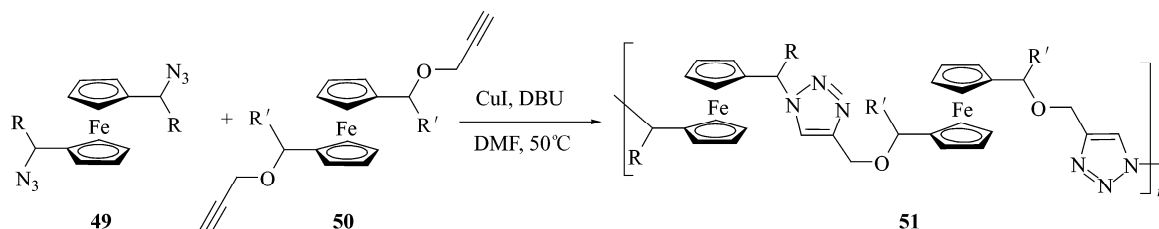
48 is viscous gum. DSC experiments show that incorporation of the aromatic units and the polar triazole moiety is enough to reversibly crosslink the poly(siloxane) physically, whereas, aliphatic block does not lead to network formation.



Scheme 11 Synthesis of poly(siloxane) containing PTAs
SA= sodium ascorbate, PDMS = polydimethylsiloxane

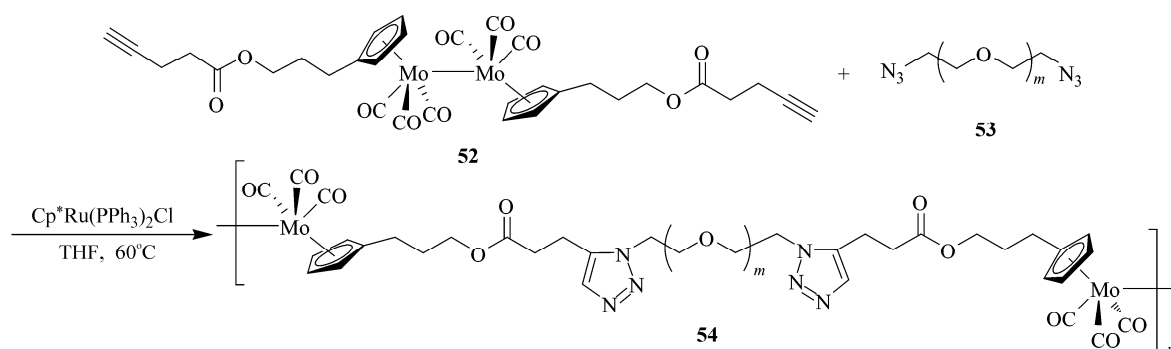
Synthesis of Organometallic PTAs

Organometallic polymers have attracted considerable attention due to their potential features such as catalytic activity, conductive and ferromagnetic properties^[44]. The Cu(I)-catalyzed click polymerization was also applied to synthesize organometallic polymers. Barner-Kowollik and coworker succeeded in preparing PTAs containing ferrocene moieties in the backbone *via* Cu(I)-catalyzed click polymerization of ferrocene-containing diazides and dialkynes^[45]. Through investigating the catalyst performance and kinetic characteristics of a model reaction of 1,1'-bis(azidoethyl)ferrocene and propargyl ether, they found that CuI and DBU catalytic system had the highest activity. The polymerizations of ferrocene containing diazides (**49**) with dialkynes (**50**) were thus carried out with such catalytic system in dry DMF at 50°C for 6 h (Scheme 12). The results show that all monomer pairs could successfully be polymerized, producing polyferrocenes **51** with high molecular weights (up to 78000). The study thus provides a pathway to polyferrocenes based on Cu(I)-catalyzed click polymerization.



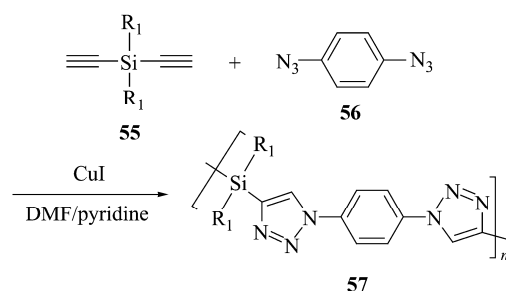
Scheme 12 Synthesis of PTAs containing ferrocene in main chain by Cu(I)-catalyzed click polymerization of diazides **49** and dialkynes **50**
DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene

Tyler and coworkers prepared PTAs with Mo-Mo bonds in the backbone by Ru-mediated click polymerization^[46]. They first explored the feasibility of Cu(I) and Ru(II)-catalyzed click reactions of dialkyne **52** with benzyl azide and 1,4-bis(azidomethyl)benzene. The model reactions showed that disproportionation of the Mo-Mo bond occurred prior to the completion of Cu(I)-catalyzed click reaction. Whereas, the Ru(II)-catalyzed click reaction can be completed in 4 h with no Mo-Mo bond disproportionation occurred. Dialkyne **52** and diazide **53** were thus subjected to click polymerization with the catalyst of $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ in THF at 60°C for 15 h (Scheme 13). 1,5-Regioregular organometallic PTA **52** with high molecular weight (73000) was successfully obtained. This work offers a route for incorporating metal-metal bonds in the polymer backbone, such as polystyrene or poly(ethylene glycol), which are otherwise not easily accessible.



Scheme 13 Synthesis of PTAs **54** with Mo-Mo bonds in the main chain by Ru(II)-catalyzed click polymerization of dialkyne **52** and diazide **53**

Because the 3d-orbital of silicon atoms can change electron delocalization of the π -electron segments, the silicon-containing polymers have thus attracted much attention. Such polymers will possess good processability and solubility due to the flexible silicon linkers and are envisioned to exhibit unique optical properties and to be used in light-emitting devices. Feng and coworkers used the low-cost and facile Cu(I)-catalyzed click polymerization, compared to other preparation methods, to synthesize silicon-containing PTAs^[47]. The click polymerizations of diethynylsilanes **55** and 1,4-diazidobenzene **56** were carried out in DMF/pyridine mixture using CuI as catalyst at 60°C, furnishing PTAs **57** with moderate molecular weights in moderate yields (Scheme 14). The photophysical measurements show that fluorescence quantum yields of **57** are higher than that of the model compound, suggesting that the σ - π conjugation can effectively enhance the emission efficiency.



Scheme 14 Synthetic routes to silicon-containing PTAs **57** by CuI-mediated click polymerization

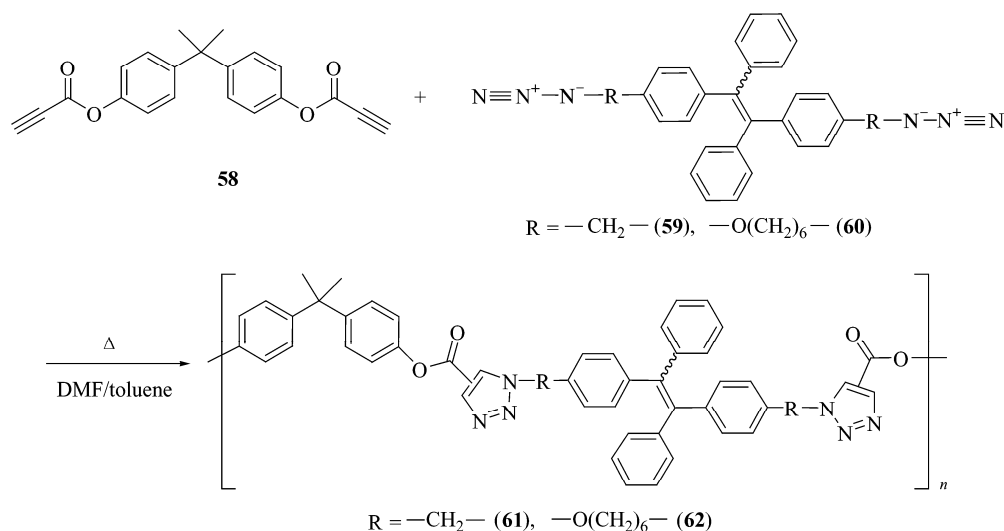
Synthesis of PTAs by Metal-free Click Polymerization

The click polymerization reactions discussed above are mediated by transition metallic catalysts. However, complete removal of the metal residue from resultant PTAs after reaction is generally difficult. The metal residues are toxic and can deteriorate the photophysical properties of the PTAs, which limit the metal-catalyzed click polymerization applications in optoelectronic devices and biomedical fields. One way to surmount this limitation is to develop nonmetallic or metal-free click polymerization.

We have established an efficient metal-free click polymerization of bis(arylacetylene)s and diazides^[48, 49]. The preparation of aryylacetylene monomers, however, requires many reaction steps and harsh reaction conditions^[50, 51]. More recently, we succeeded in extending the alkynes used in the metal-free click polymerization from aryylacetylenes to propiolates according to the structural similarity^[52]. The propiolates can be readily prepared from commercially available propiolic acid and diols *via* a single step and one-pot esterification reaction.

Similar to the metal-free click polymerization of aryylacetylenes and azides, the reaction of 4,4'-isopropylidenediphenyl dipropiolate **58** and tetraphenylethene (TPE)-containing diazides **59** and **60** in

DMF/toluene (1:1, *V/V*) at 100°C for 6 h under nitrogen or open atmosphere can produce poly(aryloxycarbonyltriazole)s (PACT)s **61** and **62** with high molecular weight (M_w up to 23900) and regioregularities (fraction of 1,4-isomers up to *ca.* 90%) in high yields (up to *ca.* 99%) (Scheme 15).



Scheme 15 Synthesis of PACTs by metal-free click polymerization of dialkyne **58** with diazides **59** and **60**

Thanks to the incorporated TPE unit, which exhibits the unique feature of aggregation-induced emission (AIE)^[53, 54], the PACTs are also AIE-active. As shown in Fig. 2(a), PTA **61** is almost nonemissive in THF but induced to emit intensely by gradually formed aggregates in THF/water mixtures. The variation in the quantum yields (Φ_F) of **61** and **62** in THF/water mixtures with different water fractions further verifies their AIE characteristics (Fig. 2b).

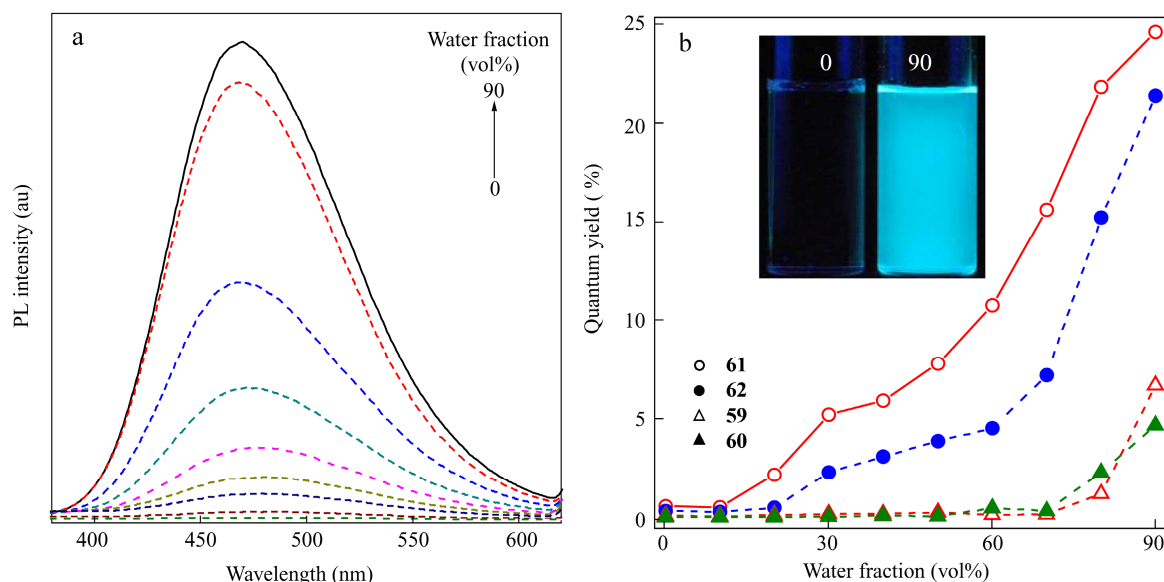


Fig. 2 (a) PL spectra of **61** in THF and THF/water mixtures; (b) Variation in the quantum yields (Φ_F) of **61**, **62** and their monomers **59** and **60** in THF/water mixtures with different water fraction
Inset: photographs taken under illumination of a hand-held UV lamp

By taking advantage of the AIE feature of **61** and **62**, their nanoaggregates in THF/water mixture with water fraction of 90% can be acted as fluorescent sensors to detect explosives, such as picric acid (PA) (Fig. 3)^[55]. Progressive addition of PA into the aggregate suspension of **61** caused gradual decrease in its emission intensity (Fig. 3a). The detection limit of PA could be lowered down to 1 $\mu\text{g/mL}$. The Stern-Volmer plots of **61** and **62** keep linear when their concentrations are below 20 $\mu\text{g/mL}$, afterwards, the curves of **61** and **62** bend upward. The quenching behavior of TPE nanoaggregates gives a nearly straight line. The control experiments indicate that the quenching of the nanoaggregates of **61** and **62** by PA is superamplified (Fig. 3b). The energy transfer from the excited states of the polymer nanoaggregates to the ground state of PA was ascribed to the mechanism of the quenching effect.

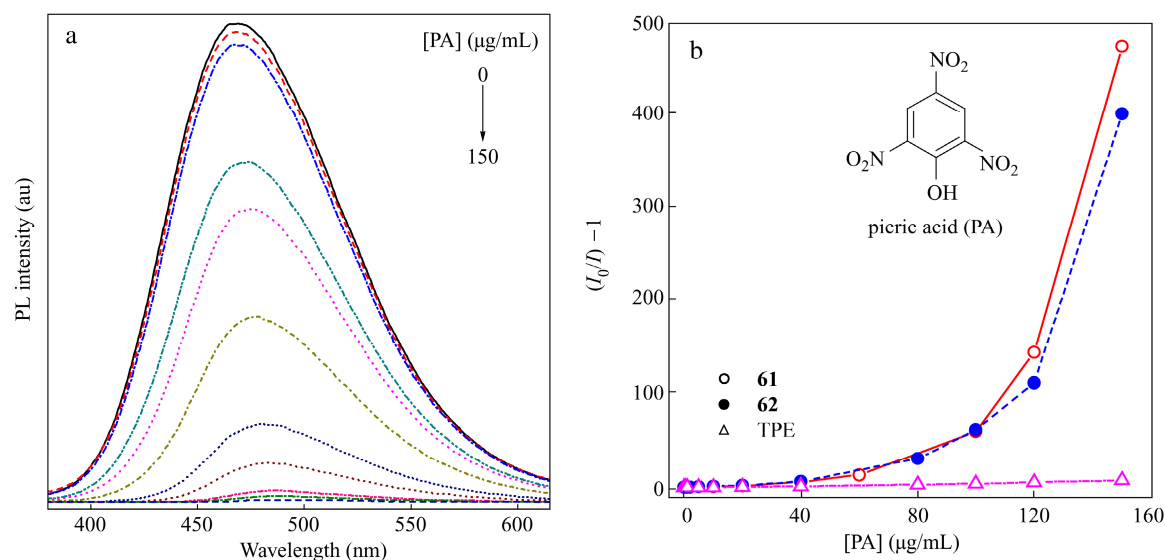
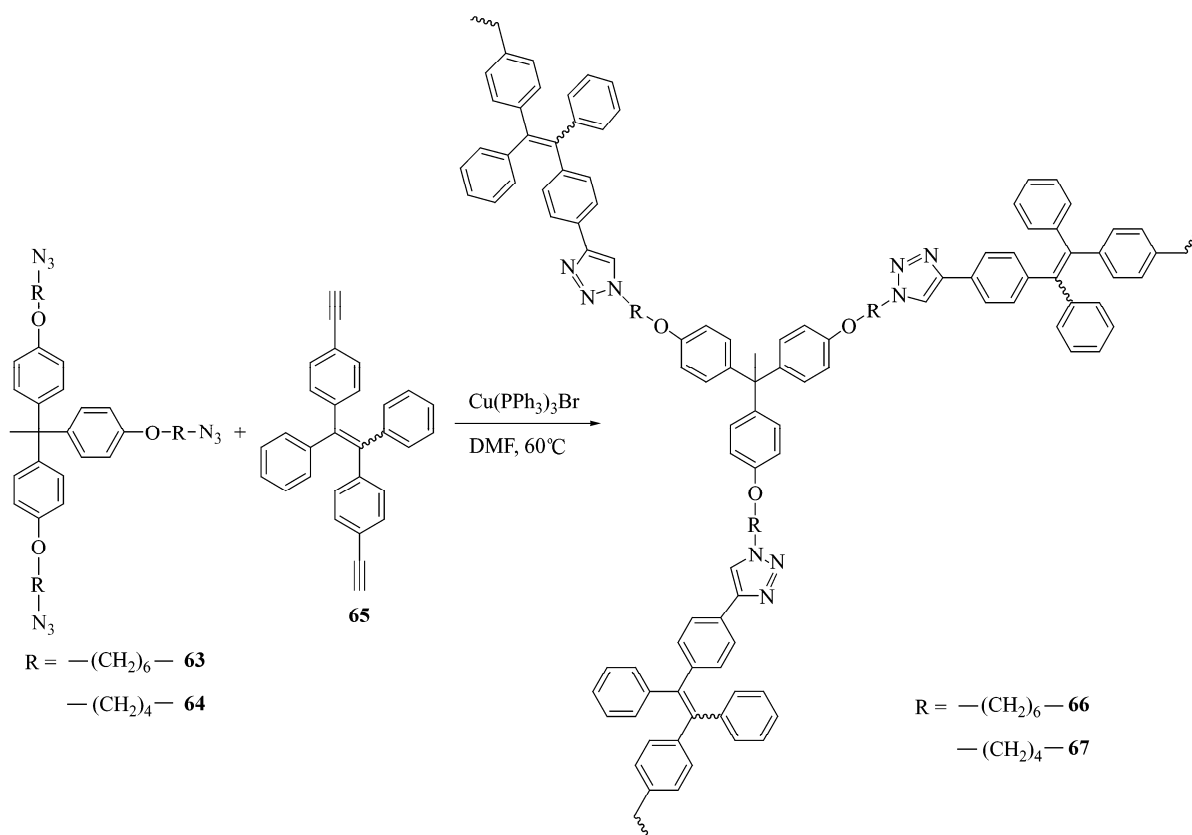


Fig. 3 (a) PL spectra of **61** in THF/water mixtures (f_w : 90%) containing different amounts of picric acid (PA); (b) Stern-Volmer plots of $(I_0/I) - 1$ of **61**, **62** and TPE versus PA concentration I = peak intensity and I_0 = peak intensity at $[\text{PA}] = 0 \mu\text{g/mL}$

PTAs WITH HYPERBRANCHED STRUCTURES

Though most of the researches on the click polymerization have been focused on preparation of PTAs with linear structures, there are some reports about synthesis of PTAs with hyperbranched structures since our reviews^[18, 19, 56].

On the basis of our recent results on preparation of hyperbranched PTAs (*hb*-PTAs)^[57], we successfully synthesized AIE-active *hb*-PTAs with spring-like architectures from the $A_2 + B_3$ monomer pairs by the organosoluble $\text{Cu}(\text{PPh}_3)_3\text{Br}$ -mediated click polymerization^[58]. The reactions of triazides (**63** and **64**) with **65** were carried out in DMF at 60°C in the presence of $\text{Cu}(\text{PPh}_3)_3\text{Br}$ (Scheme 16), producing soluble *hb*-PTAs **66** and **67** with satisfactory molecular weights (M_w up to 12400) in high yields (up to 88.3%) after 5–7 h. **66** and **67** with flexible alkyl chains possess good film-forming abilities and show high optical transparency in their film states, making them promising for photonic applications. Thanks to the contained TPE moieties and spring-like architectures, **66** and **67** are nonemissive in their THF solutions, but emit intensely in their aggregate states, demonstrating the AIE characteristics.



Scheme 16 Synthesis of *hb*-PTAs **66** and **67** by Cu(I)-catalyzed click polymerization of triazides **63** and **64** with dialkyne **65**

The nanoaggregates of **61** and **62** can also act as chemosensor to detect explosives. The responsive optical properties of the *hb*-PTAs upon addition of PA and 2,4,6-trinitrotoluenen (TNT) were investigated by fluorescence spectra. The emission intensities of *hb*-PTAs decrease progressively with gradual addition of the explosives but without change of their spectral profiles. When the concentrations of PA and TNT are below 0.09 and 1.0 mmol/L, the Stern-Volmer plots of **61** and **62** are linear. Afterwards, both plots bend upward, indicative of superamplified quenching effect (Fig. 4)^[59]. It is noticed that the quenching of the aggregates emission is more sensitive by PA than that by TNT. From the UV and PL spectra and cyclic voltammetry measurement, such behaviors are concluded to be mainly caused by different mechanism. The quenching of polymer aggregates by PA is energy transfer, and that by TNT is charge transfer.

Li and coworkers prepared six *hb*-PTAs containing nonlinear optical chromophores by the Cu(I)-catalyzed click polymerization^[60]. The reactions of AB₂-type monomer **68** were carried out in DMF/water (20:1, *V/V*) under a nitrogen atmosphere at room temperature using CuSO_4/SA as the catalyst for 16 h (Scheme 17), producing pristine PTAs rich of azido groups in their periphery. These pristine PTAs were then end-capped with six monoynes **69** by the click reaction, furnishing six *hb*-PTAs **70** with high molecular weights (M_w up to 259000). **70** are soluble in polar solvents of DMF and DMSO. Thanks to their bulky end-capping groups, **70d–70f** are also soluble in THF, chloroform *etc.* The optical nonlinearity measurements showed that **70d** with carbazole end-capping groups has the best performance, indicating that carbazole group is the optimal isolation group for polymer **70**. Furthermore, the orientation stabilities of **70** can also be tuned by end-capping groups. The nonlinear optical performance of polymers **70** makes them promising for practical photonic applications.

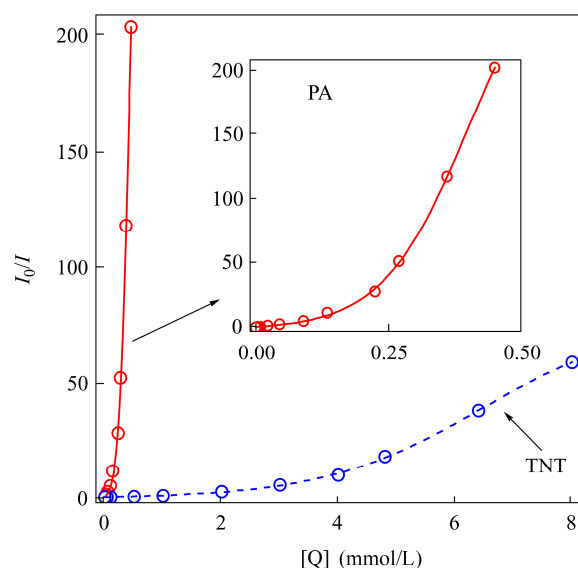
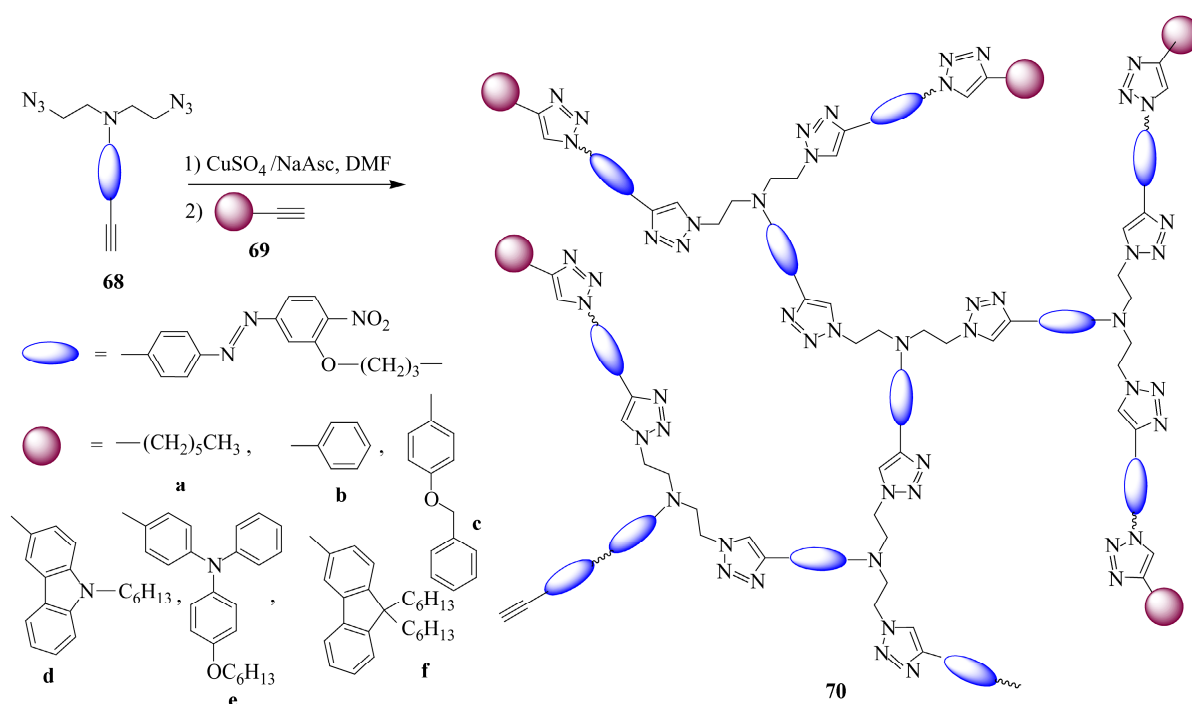


Fig. 4 Stern-Volmer plots of I_0/I versus [PA] in THF/water with water fraction of 90% and [TNT] in THF/methanol with methanol fraction of 90% (Reproduced with permission from Ref. [58]. Copyright 2011, Royal Society of Chemistry)
Inset: enlarged plot of I_0/I versus [PA]; [Q] represents the concentration of PA and TNT; I = peak intensity and I_0 = peak intensity at [Q] = 0 mmol/L



Scheme 17 Synthetic routes of *hb*-PTAs **70** by Cu(I)-catalyzed click polymerization

CONCLUSIONS AND OUTLOOK

Azide-alkyne click polymerization has made rapid progress in recent years. The Cu(I)- and Ru(II)-mediated click polymerizations produce 1,4- and 1,5-regioregular PTAs, respectively. Different from the conventional Huisgen 1,3-dipolar polycycloaddition of azide and alkyne, the thermal activated click polymerization of

propiolate and azide provides polymers with 1,4-isomer fraction up to *ca.* 90%. Thus, this reaction is a kind of metal-free click polymerization. By modifying the synthetic routes and optimizing polymerization conditions, researchers have obtained a novel class of linear and hyperbranched PTAs with high molecular weights, good solubility and thermal stability, and unique functional properties, such as aggregation-induced emission, optical nonlinearity and biodegradability. Furthermore, the produced triazole moieties in PTA are not only used as linkers, but also play key roles in polymer functionality. For example, their ability to bind metal ions makes the PTAs show excellent fluorescence response for metal ions detection.

Although great progress has been achieved, further development of click polymerization is still full of challenges. The possible opportunity will be design of new functional and active monomers, exploration of new efficient catalytic systems, generation of novel advanced functional properties and so on. It is anticipated that with the enthusiastic efforts of polymer scientist, the click polymerization will become a versatile and powerful tool for the synthesis of new PTAs with well-defined molecular structures and advanced functional properties.

REFERENCES

- 1 Rostovtsev, V.V., Green, L.G., Fokin, V.V. and Sharpless, B.K., *Angew. Chem. Int. Ed.*, 2002, 41(14): 2596
- 2 Tornøe, C.W., Christensen, C. and Meldal, M., *J. Org. Chem.*, 2002, 67(9): 3057
- 3 Carlmark, A., Hawker, C., Hult, A. and Malkoch, M., *Chem. Soc. Rev.*, 2009, 38(2): 352
- 4 Chu, C.H. and Liu, R.H., *Chem. Soc. Rev.*, 2011, 40(5): 2177
- 5 Tasdelen, M.A., Kahveci, M.U. and Yagci, Y., *Prog. Polym. Sci.*, 2011, 36(4): 455
- 6 Lau, Y.H., Rutledge, P.J., Watkinson, M. and Todd, M.H., *Chem. Soc. Rev.*, 2011, 40(5): 2848
- 7 Fu, R. and Fu, G.D., *Polym. Chem.*, 2011, 2(3): 465
- 8 Hein, J.E. and Fokin, V.V., *Chem. Soc. Rev.*, 2010, 39(4): 1302
- 9 Amblard, F., Cho, J.H. and Schinazi, R.F., *Chem. Rev.*, 2009, 109(9): 4207
- 10 Iha, R.K., Wooley, K.L., Nystrom, A.M., Burke, D.J., Kade, M.J. and Hawker, C.J., *Chem. Rev.*, 2009, 109(11): 5620
- 11 Meldal, M. and Tornøe, C.W., *Chem. Rev.*, 2008, 108(8): 2952
- 12 Liu, Z., Sun, J. and Hu, J., *Acta Polymerica Sinica (in Chinese)*, 2010, (6): 705
- 13 Golas, P.L. and Matyjaszewski, K., *Chem. Soc. Rev.*, 2010, 39(4): 1338
- 14 Binder, W.H. and Sachsenhofer, R., *Macromol. Rapid. Commun.*, 2008, 29(12-13): 952
- 15 Goodall, G.W. and Hayes, W., *Chem. Soc. Rev.*, 2006, 35(3): 280
- 16 Qin, A., Jim, C.K.W., Lam, J.W.Y., Sun, J. and Tang, B.Z., *Chinese J. Polym. Sci.*, 2009, 27(2): 145
- 17 Scheel, A.J., Komber, H. and Voit, B., *Macromol. Rapid. Commun.*, 2004, 25(12): 1175
- 18 Qin, A., Lam, J.W.Y. and Tang, B.Z., *Chem. Soc. Rev.*, 2010, 39(7): 2522
- 19 Qin, A., Lam, J.W.Y. and Tang, B.Z., *Macromolecules*, 2010, 43(21): 8693
- 20 Mcquade, D.T., Pullen, A.E. and Swager, T.M., *Chem. Rev.*, 2000, 100(7): 2537
- 21 Yu, W., Liu, B., Pei, J., Zeng, G. and Huang, W., *Chinese J. Polym. Sci.*, 2001, 19(6): 603
- 22 Kraft, A., Grimsdale, A.C. and Holmes, A.B., *Angew. Chem. Int. Ed.*, 1998, 37(6): 403
- 23 van Steenis, D.J.V.C., David, O.R.P., van Strijdonck, G.P.F., van Maarseveen, J.H., and Reek, J.N.H., *Chem. Commun.*, 2005, (34): 4333
- 24 Chen, Z., Dreyer, D.R., Wu, Z., Wiggins, K.M., Jiang, Z. and Bielawski, C.W., *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49: 1421
- 25 Huang, X., Dong, Y., Meng, J., Cheng, Y. and Zhu, C., *Synlett*, 2010, (12): 1841
- 26 Huang, X., Meng, J., Dong, Y., Cheng, Y. and Zhu, C., *Polymer*, 2010, 51(14): 3064
- 27 Zheng, L., Huang, X., Shen, Y. and Cheng, Y., *Synlett*, 2010, (3): 453
- 28 Nagao, Y. and Takasu, A., *J. Polym. Sci., Part A: Polym. Chem.*, 2010, 48: 4207
- 29 Ameduri, B. and Boutevin, B., "Well-architected fluoropolymers: synthesis, properties and applications", Elsevier, Amsterdam, 2004, p. 103

- 30 Soules, A., Ameduri, B., Boutevin, B. and Calleja, G., *Macromolecules*, 2010, 43(10): 4489
- 31 Zhou, X., Du, L., Wan, L., Wang, X.E.Y. and Huang, F., *Bull. Korean Chem. Soc.*, 2010, 31(9): 2603
- 32 Ye, Y., Yen, Y., Cheng, C., Syu, Y., Huang, Y. and Chang, F., *Polymer*, 2010, 51(2): 430
- 33 Binauld, S., Fleury, E. and Drockenmuller, E., *J. Polym. Sci., Part A: Polym. Chem.*, 2010, 48: 2470
- 34 Sheng, X., Mauldin, T. and Kessler, M., *J. Polym. Sci., Part A: Polym. Chem.*, 2010, 48: 4093
- 35 Liu, X., Quan, L., Tian, J., Laquer, F., Ciborowski, P. and Wang, D. *Biomacromolecules*, 2010, 11(10): 2621
- 36 Wang, Y., Zhang, R., Xu, N., Du, F., Wang, Y., Tan, Y., Ji, S., Liang, D. and Li, Z., *Biomacromolecules*, 2011, 12(1): 66
- 37 Guo, J., Wei, Y., Zhou, D., Cai, P., Jing, X., Chen, X. and Huang, Y., *Biomacromolecules*, 2011, 12(3): 737
- 38 Besset, C., Pascault, J., Fleury, E., Drockenmuller, E. and Bernard, J., *Biomacromolecules*, 2010, 11(10): 2797
- 39 Eissa, A. and Khosravi, E., *Eur. Polym. J.*, 2011, 47(1): 61
- 40 Tsarevsky, N.V., Sumerlin, B.S. and Matyjaszewski, K., *Macromolecules* 2005, 38 (9): 3558
- 41 Ates, S., Durmaz, Y., Torun, L. and Yagci, Y., *J. Macromol. Sci., Part A*, 2010, 47(8): 809
- 42 Durmaz, H., Dag, A., Hizal, G. and Tunca, U., *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49: 1195
- 43 Schmidt, U., Zehetmaier, P.C. and Rieger, B., *Macromol. Rapid Commun.*, 2010, 31, 545
- 44 Abdelaziz, A. and Manners, I., "Frontiers in metal-containing polymers", Wiley-Interscience, New Jersey, 2007, p. 123
- 45 Lang, C., Voll, D., Inglis, A., Dingenouts, N., Goldmann, A., Barner, L. and Barner-Kowollik, C., *Macromol. Chem. Phys.*, 2011, 212(8): 831
- 46 Brady, S., Shultz, G. and Tyler, D., *J. Inorg. Organomet. Polym.*, 2010, 20(3): 511
- 47 Wang, Y., Wang, D., Han, J. and Feng, S., *J. Organomet. Chem.*, 2011, 696: 1874
- 48 Qin, A., Jim, C.K., Lu, X., Lam, J.W.Y., Haeussler, M., Dong, Y., Sung, H.H.Y., Williams, I.D., Wong, G.K.L. and Tang, B.Z., *Macromolecules*, 2007, 40(7): 2308
- 49 Qin, A., Tang, L., Lam, J.W.Y., Jim, C.K., Yu, Y., Zhao, H., Sun, J. and Tang, B.Z., *Adv. Funct. Mater.*, 2009, 19(12): 1891
- 50 Dong, H.C., Zheng, R.H., Lam, J.W.Y., Haeussler, M. and Tang, B.Z., *Macromolecules*, 2005, 38(15): 6382
- 51 Qin, A.J., Lam, J.W.Y., Dong, H.C., Lu, W.X., Jim, C.K.W., Dong, Y.Q., Haeussler, M., Sung, H.H.Y., Williams, I.D., Wong, G.K.L. and Tang, B.Z., *Macromolecules*, 2007, 40(14): 4879
- 52 Li, H., Mei, J., Wang, J., Zhang, S., Zhao, Q., Wei, Q., Qin, A., Sun, J. and Tang, B.Z., *Sci. China Chem.*, 2011, 54(4): 611
- 53 Luo, J., Xie, Z., Lam, J.W.Y., Cheng, L., Chen, H., Qiu, C., Kwok, H.S., Zhan, X., Liu, Y., Zhu, D. and Tang, B.Z., *Chem. Commun.*, 2001, (18): 1704
- 54 Hong, Y., Lam, J.W.Y. and Tang, B.Z., *Chem. Commun.*, 2009, (29): 4332
- 55 Qin, A., Lam, J.W.Y., Tang, L., Jim, C.K., Zhao, H., Sun, J. and Tang, B.Z., *Macromolecules*, 2009, 42(5): 1421
- 56 Liu, J.Z., Lam, J.W.Y. and Tang, B.Z., *Chem. Rev.*, 2009, 109: 5799
- 57 Qin, A., Lam, J.W.Y., Jim, C.K., Zhang, L., Yan, J., Haeussler, M., Liu, J., Dong, Y., Liang, D., Chen, E., Jia, G. and Tang, B.Z., *Macromolecules*, 2008, 41(11): 3808
- 58 Wang, J., Mei, J., Yuan, W., Lu, P., Qin, A., Sun, J., Ma, Y. and Tang, B.Z., *J. Mater. Chem.*, 2011, 21(12): 4056
- 59 Liu, J.Z., Zhong, Y.C., Lu, P., Hong, Y.N., Lam, J.W.Y., Faisal, M., Yu, Y., Wong, K.S. and Tang, B.Z., *Polym. Chem.*, 2010, 1: 426
- 60 Li, Z., Wu, W., Qiu, G., Yu, G., Liu, Y., Ye, C., Qin, J. and Li, Z., *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49: 1977