



## Review

## Polymerizations based on triple-bond building blocks

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## ABSTRACT

Development of new polymerizations based on triple-bond building blocks has received considerable research attention, from which polymers with unique structures and advanced functions can be generated. In this review, we summarize the research efforts on using alkynes and nitrogen-containing triple bonds as building blocks to prepare polymers with linear and topological structures since 2010. The metathesis polymerization and polyaddition of mono- and di-substituted acetylenes, the Cu(I)-catalyzed and metal-free azide-alkyne click polymerization, the thiol-yne click polymerization, polycyclotrimerization of diynes, and the polymerizations based on cyanide and isocyanide monomers are discussed in detail. Moreover, the unique stoichiometric imbalanced polymerization based on alkynes is also briefly introduced. The functions and applications of polymers, produced from these developed polymerization reactions, such as aggregation-induced emission, self-healing, fluorescent patterning, liquid crystal, fluorescence sensing, explosive detection, chiral catalysis and gas permeability are also reviewed.

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**Abbreviations:** ACQ, aggregation-caused quenching; AEE, aggregation-enhanced emission; AIBN, 2,2'-azobisisobutyronitrile; AIE, aggregation-induced emission; APCNs, amphiphilic conetworks; ATRP, atom transfer radical polymerization; *hb*-CPTA, hyperbranched conjugated polytriazole; CuAAC, Cu(I)-catalyzed alkyne-azide click polymerization; DB, degree of branching; DCM, dichloromethane; DMF, *N,N*-dimethyl formamide; DMPA, 2,2-dimethoxy-2-phenylacetophenone; DMSO, dimethylsulfoxide; DSC, differential scanning calorimetry; GPC, gel permeation chromatography; HPS, hexaphenylsilole; HCPE, hyperbranched conjugated polyelectrolyte; MCR, multicomponent reaction; MFAACP, metal-free alkyne-azide click polymerization;  $M_n$ , number-average molecular weights; MPA,  $\alpha$ -methoxy phenylacetic acid;  $M_w$ , weight-average molecular weight; NMR, nuclear magnetic resonance; PA, polyacetylene; PATA, poly(aroyltriazole); PACT, poly(aroxycarbonyltriazole); PCL, poly(3-caprolactone); PDI, polydispersity index; PDPA, poly(diphenylacetylene); PDMS, poly(dimethylsiloxane); PE, polyethylene; PEG, polyethylene glycol; PFP, pentafluorophenyl; PMCD, permethylated  $\alpha$ -cyclodextrin; PMDETA, *N,N,N',N'*-pentamethyldiethylene triamine; PL, photoluminescence; PP, polypropylene; PPA, poly(1-phenyl-1-alkyne); PTA, poly(1,2,3-triazole); PVC, polyvinyl chloride; RAFT, reversible addition-fragmentation chain transfer; ROMAP, ring-opening metathesis alkyne polymerization; RI, refractive index; RIM, restriction of intramolecular motion; PVS, poly(vinylsulfide); SA, sodium ascorbate; SEM, scanning electron microscope; SWNTs, single-walled carbon nanotubes; THF, tetrahydrofuran; TCP, three-component polymerization; TPE, tetraphenylethene.

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## 1. Introduction

Polymers are giant molecules built up of simple repeating units. In nature, there are many natural polymers, such as protein consisting of amino acid, cellulose consisting of glucose, rubber, and so on. As early as 1839, Simon observed that styrene could change from liquid to solid upon heating. However people had no idea of what happened to the styrene at that time. Not until 1920s when Staudinger proposed the concept of “macromolecules”, which was established by Carothers and other researchers later, did scientists understand this issue. These ingenious works in the early 20th century laid a solid foundation for modern polymer science.

According to the mechanism, polymerizations can be divided into two parts: step- and chain-growth reactions. A typical polymerization via step-growth mechanism is condensation polymerization. Polymeric materials like phenolics, amino resins, polyesters, polycarbonates, polyamides, etc. are all synthesized via condensation polymerizations from bifunctional monomers. The general feature of these polymerizations is that the monomers are polymerized through eliminating low molecular weight molecules like water. On the other hand, polymers such as polyethylenes (PEs), polypropylenes (PPs), polyvinyl chlorides (PVCs) are polymerized via chain-growth polymerizations. During the reactions, the monomers are initiated by heating, radiation or initiator, and the carbon–carbon double bonds are opened and connected to form main-chains. Repeating this process readily generates macromolecules.

The polymers discussed above are constructed from carbon–carbon double-bond building blocks and their main-chains comprise saturated carbon–carbon single bonds, making these polymers electronically inactive. However, the polymers prepared from carbon–carbon (nitrogen) triple-bond building blocks are linked with electronically unsaturated double bonds, endowing them with versatile optoelectronic properties. Moreover, the carbon–carbon (nitrogen) triple-bond building blocks are rich in monomer types such as alkyne, cyanide, and isocyanide, and polymerization reactions, such as metathesis polymerization, polycyclization, and polyaddition. Polyacetylenes (PAs), polyphenylacetylenes (PPAs), polyarylenes and polytriazoles (PTAs) with linear and hyperbranched structures can be readily prepared through these polymerizations. Thanks to the robust nature of the polymerizations based on carbon–carbon (nitrogen) triple-bond building blocks, and enthusiastic and fruitful efforts devoted by polymer scientists, a variety of novel polymers with versatile properties have been produced. These properties include liquid crystallinity, chiroptical activity, magnetic susceptibility, electrical conductivity, photoconductivity, luminescence, fluorescence sensing, refractivity, optical nonlinearity, gas permeability, biological activity and photochemical pattern formation and so on.

Several excellent reviews on specific functional polymers based on carbon–carbon triple bonds, *i.e.* alkynes have already been published [1–14]. In 2009, we also comprehensively overviewed the progress on the syntheses, structures, and properties of acetylene

polymers [15]. Thus, this review mainly summarizes the developments on polymer syntheses and functions in this area since 2010.

## 2. Metathesis polymerization

### 2.1. Metathesis polymerization of substituted acetylenes

PAs were initially synthesized by Natta et al. using a Ti-based catalyst in 1958. This non-substituted PA, however, is insoluble, making it difficult in processing. However, the carbon–carbon alternating double bonds in its main-chains imply that it is a promising candidate showing unique properties, such as high-temperature superconductivity. Indeed, in the late 1970s, Heeger, Shirakawa and MacDiarmid discovered the electrical conductivity in the PA films upon doping [16]. The break-through work made by them lent a strong impetus to the research on acetylenic polymers and shed a light on the world [17,18].

With the Ti-based catalysts, unfortunately, substituted acetylenes cannot be polymerized [19,20]. In 1974, Masuda and Higashimura found that phenylacetylene could be polymerized in the presence of  $WCl_6$  or  $MoCl_5$ . PPAs with number-average molecular weights ( $M_n$ ) up to 15,000 were obtained [21]. Polymerization of acetylenes using a Ti-based catalyst propagates with an insertion mechanism, whereas  $WCl_6$  or  $MoCl_5$  catalyzed ones undergo via a metathesis mechanism, whereby the active species are metal carbenes [22,23]. Later, Masuda found that a small amount of organometallic cocatalyst of  $Ph_4Sn$  or  $n-Bu_4Sn$  can distinctly accelerate this polymerization [24]. After this discovery, many classic metathesis catalysts, representatively  $TaX_5$ ,  $NbX_5$  ( $X = F, Cl, Br$ ) [25–28],  $M(CO)_xLy$  ( $M = Mo, W$ ) [29,30], Schrock's catalysts [31,32], were developed for the synthesis of substituted PAs bearing pendant functional groups, which offer the PAs to exhibit an array of unique properties, such as electrical conductivity, liquid crystallinity, light emission, fluorescence sensing, optical nonlinearity, chiral recognition, light refraction, thermochromism, biological activity, patterning and imaging [33,34]. In this section, we mainly survey the metathesis polymerization of substituted acetylenes and their properties after Masuda's work [22].

It's very important to select proper catalytic system for a certain polymerization because it will significantly influence the yield, molecular weight, and solubility *etc.* of the product. One of the examples is demonstrated by Sakaguchi and coworkers. They polymerized various 1-alkyl-2-arylacetylenes **1a–1d** in the presence of the catalytic system of  $NbCl_5/n-Bu_4Sn$ ,  $TaCl_5/n-Bu_4Sn$ , or  $WCl_6/Ph_4Sn$  (Scheme 1) [35,36]. Interestingly,  $NbCl_5$ -catalyzed polymerization of **1a–1d** can produce PAs **2a–2d** with higher molecular weights in higher yields than those catalyzed by  $TaCl_5$  or  $WCl_6$ . Moreover, PA **2b** produced by the  $NbCl_5$ -catalyzed polymerization of **1b** is soluble in methanol. However, if the polymerizations are catalyzed by  $TaCl_5/n-Bu_4Sn$  or  $WCl_6/Ph_4Sn$ , the resultant polymers become insoluble in methanol.

Furthermore, the monomer structures will also affect the polymerization results. Helical disubstituted polyacetylene **3a** was

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