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# Poly(disubstituted acetylene)s: Advances in polymer preparation and materials application

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ABSTRACT

Conjugated polymers (CPs) have drawn great attention due to their excellent optical and electronic properties for decades. Among the varieties of CPs, polyacetylenes (PAs) triggered a revolution in polymer science due to their conductivity in highly doped state. Yet, the unstability and unprocessability of the pristine polyacetylene led researchers exploring their derivatives with substituents. Luckily, greatly improved stability and processability have been achieved by poly(disubstituted polyacetylene)s or PDSAs, that show efficient fluorescence emission in both solution and solid state and excellent circular polarized luminescence. This review summarizes recent research regarding PDSAs, beginning with the novel achievements of the discovery of the Pd-based catalyst systems for the polymerization of disubstituted acetylene monomers (DSAms), followed by a description of the effect of polymerization catalysts on the stereochemistry of obtained polymers and the effect of the stereochemistry on functional properties. Then, an updated summary of alternative synthetic routes to PDSAs, that is, post-polymerization modifications is contributed. This strategy has shown strong vitality due to the highly efficient reaction tools furnished by organic chemists such as click chemistry and activated esters. PDSAs usually possess intrinsically porous structure, exhibiting significant and variable fluorescent responses to exotic species such as solvents with different polarities, metal cations and explosives, and these properties indicate that PDSAs are promising candidates for fluorescent sensors and probes. Their reversible responses to applied fields such as stress and fluid gradient allow PDSAs to be active components of actuators. Moreover, due to the unique conjugated polyene main-chain and metathesis polymerization mechanism, PDSAs pronounced chirality transfer capacity and outstanding circular polarized luminescent property. Finally, an outlook of the application and suggestions of the synthetic efforts are forwarded.



**Contents**



*Abbreviations:* BOPP, biaxially oriented polypropylene; CD, circular dichroism; CPE, conjugated polyelectrolyte; CPL, circular polarized luminescence; CPs, conjugated polymers; CT, charge transfer; DMSO, dimethylsulfoxide; DNT, 2,6-dinitrotoluene; DSAm, disubstituted acetylene monomer; EWG, electron withdrawing group; FFV, fractional free volume; FL, fluorescence; IaSS, intramolecular stacked structure; LC, liquid crystal; MWCNTs, multi-walled carbon nanotubes; N-LC, nematic liquid crystal; N*-LC, chiral nematic liquid crystal; NR, Nile red; PCM, phase change materials; PDSAs, poly (disubstituted acetylene)s; PL, photoluminescence; PMSAs, poly(mono-substituted acetylenes); PO, paraffin oil; SCA, silane coupling agent; SIFC, surfactant induced fluorescence change; SmA, smectic A phase; WAXD, wide angle X-ray diffraction; μCP, microcontact printing.

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## 1. Introduction

The discovery of conductivity in doped polyacetylene by Heeger, MacDiarmid and Shirakawa et al. opened a new era of polymer science [1–3]. The concept of a 'conducting polymer' changed the traditional notion that polymers are insulators, motivating efforts to explore other conductive polymers. As a result, a new branch of polymer science, *i.e.*, conjugated polymers (CPs) emerged, a variety of CPs such as polydiacetylenes (PDAs) [4–6], poly(*para*phenylenes) (PPPs) [7–9], polyfluorenes (PF) [10,11], poly(phenylene vinylenes) (PPVs) [12–14], poly (*para*-phenyleneethynylene)s [15,16], and hetero-atom containing species [e. g., poly(thiophenes), polypyrroles, polyanilines and poly(benzothiazoles)] have been designed and prepared. These CPs exhibit intriguing optical/photonic and electric/electronic properties, with applications in polymeric light emitting and displaying devices, polymer-based photovoltaic cells, nonlinear optical materials and polymeric fluorescent probes and sensors, attracting both academic research and industrial interests.

Polyacetylenes (PAs), as the archetypal conjugated polymer have, however, received less attention in recent years. The basic drawbacks, in comparison with newly reported CPs, are low stability and poor processability. To overcome these, substituents are introduced to PAs. The substitution groups effectively separate the distance between adjacent polyene chains and reduce interchain π-π interaction, providing improved solution processability to the derivatives. However, the reduction of interchain π-π interaction destroyed the potential electric conductivity of the substituted PAs. Fortunately, by incorporating functional groups into the substituents, the resulted PAs were endowed with various functions such as liquid crystal [17–22], gas permeability [23–26], chirality transfer [27], fluorescence (FL) properties [28–39] and so on [40–43]. With bulky substitution groups, the thermal and chemical stability of the corresponding polymers are enhanced due to protection of the side groups on the reactive polyene mainchain [44].

Multi-functional PAs and poly(disubstituted acetylene)s (PDSAs) demonstrate some advantages over the non- and mono-substituted counterparts. Specifically, PDSAs usually have higher thermal stability, better chemical resistance, dramatically enhanced FL emitting capacity. However, the polymerization of the disubstituted acetylene monomers (DSAms) is difficult, especially for DSAms bearing polar groups, only a few DSAms have been polymerized. Since catalysts play a key role in the polymerization, research explored efficient catalyst systems as well as co-catalysts towards DSAms in the past decade [45–49]. There are tutorial reviews by Masuda and Tang et al. [50,51] on the use of the classical transition metal catalysts of Mo, W, and Ta together with co-catalysts such as $Ph_4Sn$ and $Bu_4Sn$ and most research groups involved in the polymerization of DSAm have used these traditional catalysts [52–57]. Although Mo-, W-, and Ta-based catalysts are effective in some cases, their tolerance to moisture and polar groups is poor. This disadvantage, obviously, limited further development and practical applications greatly.

Since the direct polymerization of DSAms carrying high polar functional groups is formidable if not impossible, researchers turned to develop PDSA-based polymer precursors and further modify them with functional groups [58–61]. The post-polymerization modification route through PDSA precursors with emerging powerful synthetic tools such click chemistry, activated ester strategy, Michael addition has been popular in preparation of functional PDSAs [62]. Using post-polymerization modification strategy, the property of modified polymers can be pre-designed and controlled. In addition, it was found that PDSAs with bulky substitution groups, especially poly(diphenyl-substituted acetylenes), efficiently emit FL, both in solution and in solid state [63]. This property facilitates the use of PDSAs as a fluorescent tool [42,57]. Combined with smart design, the PDSAs reported in recent years demonstrate promising and fascinating performance in many practical applications [64–66]. The following summarizes the development of novel catalysts towards the polymerization of DSAms, the post-polymerization modification methods to prepare functional PDSAs and the application of PDSAs as functional materials and active components since 2010.

## 2. Novel polymerization catalyst systems and the regio-regularity of the derived PDSAs

### 2.1. Palladium-based polymerization catalyst systems

Due to their promising properties, PDSAs have attracted much attention in recent years [67–69] and great efforts on the preparation of functional PDSAs from DSAms were made by the Masuda and Tang groups [50,51,62,70,71]. The early transition metal catalyst systems gave high molecular weight resultants and a trans-rich conformation in the PDSA main chain. However, W, Mo, and Ta-based catalyst systems have shown very high sensitivity to oxygen and polar groups, thus only limited kinds of DSAms can be