

# Synthesis of acetylene-based widely conjugated polymers by metathesis polymerization and polymer properties

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## Abstract

Studies on the polymerization of monosubstituted acetylenes with condensed aromatic rings are surveyed, and a new concept is demonstrated for designing acetylenic monomers to provide widely conjugated polymers with excellent solubility and stability. Monosubstituted acetylenes with condensed aromatic rings, which is designed to possess large steric hindrance between the pendant groups and main chain of the formed polymers, have been proven to give widely conjugated polymer backbones. W catalysts are advantageous for the production of polymers with high solubility and expanded main-chain conjugation, while Mo and Rh catalysts offer insoluble polymers with low degree of conjugation. Based on these results, a new substituted arylacetylene, anthrylacetylene with alkoxy carbonyl group (**2**), was subjected to polymerization to create a widely conjugated polymer with high molecular weight, excellent solubility and stability as well as film-forming ability. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Metathesis polymerization; Transition-metal catalyst; Substituted acetylene; Substituted polyacetylenes; Widely conjugated polymer; Condensed aromatic ring

## 1. Introduction

One of the recent attentions in the field of polymer science has been paid to the conjugated polymers due to their characteristic optical, electrical and magnetic properties [1]. Tremendous advances are readily found in the discovery of new conjugated polymers, in the improvement of their preparative methods, and also in tailoring their properties. These developments have undoubtedly originated from the finding of conductivity as high as that of copper

metal in polyacetylene, which has led to the creation of a variety of conjugated polymers including poly(thiophene)s, poly(pyrrole)s, poly(*p*-phenylene)s, poly(*p*-phenylenesulphide), poly(aniline)s, and so on.

Notwithstanding the greatest contribution of polyacetylene to this new field, it is essentially impossible to apply polyacetylene as a functional material. This is simply because of the lack of processability, solubility and stability [1–3]. Extensive efforts apparently have succeeded in improving the processability by the introduction of substituents onto the polymer backbone [4,5]. However, the coplanarity of the main chain is simultaneously reduced owing to the steric repulsion between the pendant groups, which brings about poor conjugation along the

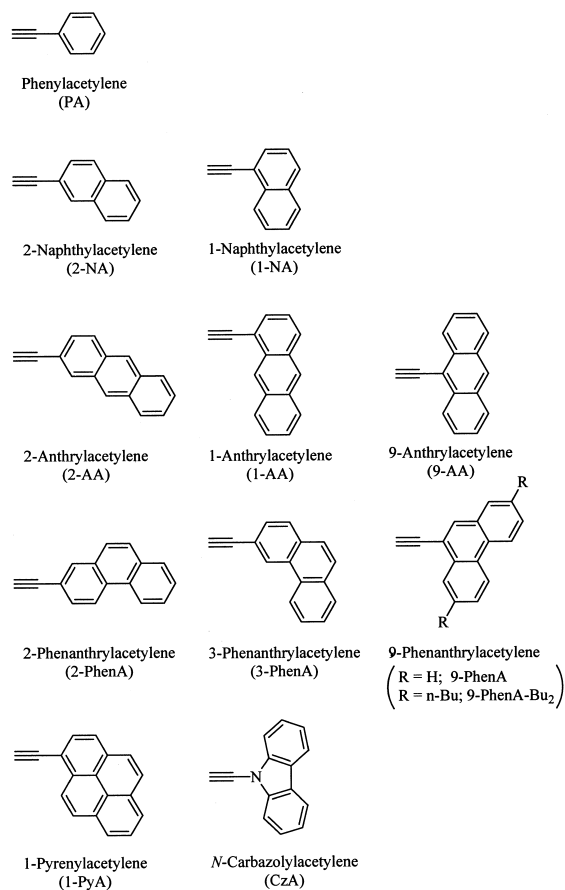
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polymer backbone. Therefore, many of high-molecular weight polymers from substituted acetylenes are colorless or only slightly colored, and show quite low unpaired-electron densities.

An answer to solve these problems was elegantly made by the cyclopolymerization of 1,6-heptadiynes that provide polymers with cyclized olefinic structure.<sup>1</sup> The presence of cyclic structure in the main chain allows the polymer backbone to exist in nearly coplanar conformation, which enables to supply widely conjugated acetylene-based polymers with good solubility and stability. Recent advances in controlling polymerization reactions also made it possible to tailor the structure of poly(1,6-heptadiynes) using well-defined metal carbene complexes [7].

In contrast, polymerization of monosubstituted acetylenes has been regarded as an ineffective route to widely conjugated polymers. This is readily recognized by the easy access to well-controlled distorted main chain, i.e., helical polyacetylenes with one-handed screw sense, by simply introducing chiral substituents [8]. However, our recent systematic study on the polymerization of a wide variety of substituted acetylenes has led to a conclusion that an appropriate design of monomers provides the polymers with high extent of conjugation from monosubstituted acetylenes. That is, arylacetylenes adequately substituted by condensed aromatic rings offer deeply colored polymeric materials [9–12]. This review article deals with recent studies on the production of widely conjugated polymers from monosubstituted acetylenes with a variety of condensed aromatic rings (Scheme 1)<sup>2</sup>. Focuses are mainly placed on the relationship between the order of main chain conjugation and several factors such as monomer structure and catalysts. Recent suc-



cess in the production of widely conjugated acetylene-based polymers with high molecular weight as well as excellent stability and solubility is also briefly summarized.

## 2. Results

### 2.1. Naphthylacetylenes

The first example was reported by our laboratory for the polymerization of naphthylacetylene with group 6 transition-metal complexes that are the most effective catalysts for the synthesis of high-molecular weight polymers from substituted acetylenes [9]. 2-Naphthylacetylene (2-NA) polymerizes with W- or Mo-based cata-

<sup>1</sup> For a leading reference for the polymerization of 1,6-heptadiyne, see Ref. [6]. See also Refs. [4,5].

<sup>2</sup> For a review of the thermal, cationic, and Ziegler–Natta catalyzed polymerization of monosubstituted acetylenes with condensed aromatic rings, see Ref. [13].

Table 1

Selected examples for the polymerization of monosubstituted acetylenes with condensed aromatic rings

Monomer		Catalyst/Solvent	Yield (%)	$M_n$	$\lambda_{\max}^a$ (nm)	Cutoff <sup>a</sup> (nm)	Color	Ref.
Naphthylacetylene	2-NA	WCl <sub>6</sub> -MeOH/benzene	79	9000	– <sup>b</sup>	600	dark brown	[9]
		WCl <sub>6</sub> -Ph <sub>4</sub> Sn/benzene	100	9100				[9]
		MoCl <sub>5</sub> -MeOH/benzene	63	Insol.			red	[9]
	1-NA	1/cyclohexane	90	95,000	509		black	[14]
		WCl <sub>6</sub> -Ph <sub>3</sub> Bi/toluene	93	46,000	510	700	dark purple	[11]
		WCl <sub>6</sub> /dioxane	85	36,000			dark brown	[15]
		MoCl <sub>5</sub> /toluene	79	Insol.			red	[11]
		[(nbd)RhCl] <sub>2</sub> -Et <sub>3</sub> N/toluene	29	Insol.		red	[11]	
Anthrylacetylene	2-AA	WCl <sub>6</sub> -Ph <sub>3</sub> Bi/toluene	60	9000	– <sup>b</sup>	700	dark brown	[10]
	1-AA	WCl <sub>6</sub> -Ph <sub>4</sub> Sn/toluene	93 <sup>c</sup>	37,000	570	760	dark purple	[10]
		MoCl <sub>5</sub> -Ph <sub>4</sub> Sn/toluene	12 <sup>c</sup>	2400			brown	[10]
	9-AA	WCl <sub>6</sub> /toluene	62	Insol.			dark purple	[11]
Phenanthrylacetylene	2-PhenA	WCl <sub>6</sub> -Ph <sub>3</sub> Bi/toluene	55	10,000	– <sup>b</sup>	700	brown	[10]
	3-PhenA	WCl <sub>6</sub> -Ph <sub>3</sub> Bi/toluene	60	24,000	490	700	purple	[10]
	9-PhenA	WCl <sub>6</sub> -Ph <sub>4</sub> Sn/ <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	75 <sup>c</sup>	10,000	580	800	dark purple	[12]
	9-PhenA-Bu <sub>2</sub>	1/cyclohexane	100	20,000	548		black	[14]
Pyrenylacetylene	1-PyA	WCl <sub>6</sub> -Ph <sub>3</sub> Bi/toluene	67 <sup>c</sup>	6000	580	800	dark purple	[12]
<i>N</i> -Carbazolylacetylene	CzA	WCl <sub>6</sub> - <i>n</i> -Bu <sub>4</sub> Sn/toluene	35	13,000	550	740	dark purple	[16]

<sup>a</sup>In chloroform.<sup>b</sup>No absorption maximum was observed.<sup>c</sup>Partly soluble in chloroform.

lysts in benzene or chlorinated solvents (Table 1). Combined catalysts, WCl<sub>6</sub> with MeOH or Ph<sub>4</sub>Sn, provide soluble polymers in high yields, while the corresponding Mo catalysts give insoluble polymers in low yield. IR and DSC analyses indicated that the polymers obtained with MoCl<sub>5</sub> possess higher *cis* content than those prepared with W catalysts, and the insolubility of the polymers produced with Mo catalysts stems from the high *cis* content of the polymers. *Trans*-rich polymers are generally widely conjugated. Thus, poly(2-NA) obtained with W catalyst is dark brown and shows the cutoff wavelength up to 600 nm (Fig. 1), whereas, that with Mo catalyst is colored bright red.

The regioisomer of 2-NA, 1-naphthylacetylene (1-NA), was independently subjected to polymerization by Yamaguchi et al. [14], Tabata et al. [15], and us [11]. The polymerization of 1-NA with a W catalyst (**1**) gave a deeply colored polymer (black in the solid state) with  $M_n$  of 95,000 in 90% yield. Conventional W catalysts such as WCl<sub>5</sub>-Ph<sub>3</sub>Bi in toluene or

WCl<sub>6</sub> in 1,4-dioxane are also effective for the polymerization of 1-NA. Similar to the case of 2-NA, Mo-based catalysts resulted in insoluble polymers (red) in low yields. An Rh catalyst, [(nbd)RhCl]<sub>2</sub>-Et<sub>3</sub>N, that is known to provide

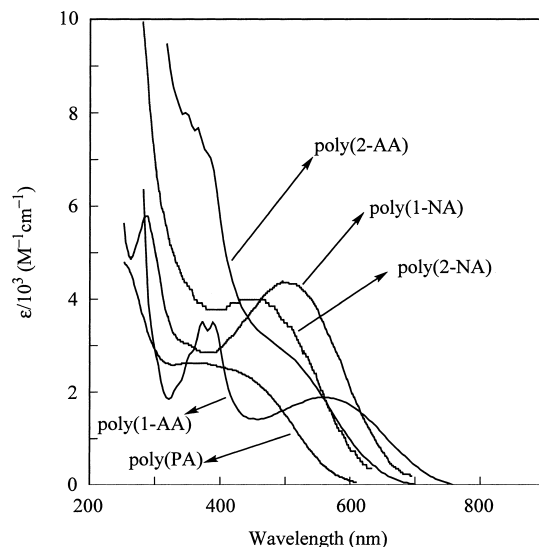


Fig. 1. UV-vis spectra of poly(1-NA), poly(2-NA), poly(1-AA), and poly(2-NA) in chloroform.

Table 2

Third order susceptibilities,  $\chi^{(3)}$ , of polyacetylenes in nonlinear optics

Polymer	$\chi^{(3)} \times 10^{12}$ (esu)	Cutoff (nm)	Ref.
<i>trans</i> -polyacetylene	5600	~ 850	[22]
poly(PA) ( <i>trans</i> )	0.54	610	[16]
poly(1-NA)	12	700	[16]
poly(1-AA)	14	740	[23]
poly(CzA)	18	740	[17]
poly(1-NA- <i>co</i> -9-AA)	40	770	[11]

stereoregular *cis*-*trans*oidal poly(phenylacetylene)s [4,5], also leads to an insoluble polymer in low yield. The most characteristic feature of poly(1-NA) is its largely red-shifted absorption compared with that of poly(2-NA). Namely, poly(1-NA) shows the absorption maximum and cutoff wavelength at 509 and 700 nm, respectively, while no absorption maximum is observed for poly(2-NA) (Fig. 1). This red-shifted absorption also contributes to the deep color (dark purple to black) and large third-order nonlinear optical susceptibility [ $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ ] of poly(1-NA) (Table 2), meaning the high order of main-chain conjugation.

## 2.2. Anthrylacetylenes

A more bulky substituent, anthryl group, was introduced to the polymer backbone to enhance the order of main-chain conjugation. We polymerized 2-anthrylacetylene (2-AA) using W catalysts to give excellent yields of soluble polymers [10]. A combination of  $WCl_6$  with  $Ph_3Bi$  is the most effective for the production of relatively high-molecular weight polymer ( $M_n = 9000$ ). In contrast to the bright color of poly(2-AA) (brown), deeply colored polymers (dark purple) are obtained from 1-anthrylacetylene (1-AA) in the presence of  $WCl_6$ -based catalysts. However, the resulting poly(1-AA) is partly insoluble in chloroform and toluene, probably due to the stiff main-chain structure. Similarly to the polymerization of naphthylacetylenes, Mo catalysts lead to low yields of the polymers with poor solubility from both 1-AA and 2-AA.

Polymerization of 9-anthrylacetylene (9-AA) was also attempted using W and Mo catalysts [11]. W catalysts give better yield than Mo catalysts, however, poly(9-AA) is unfortunately insoluble in any organic solvents regardless of the catalyst. Poly(9-AA) is a deeply colored solid (almost black in the solid state), implying the very wide conjugation of the main chain. A soluble polymer is attainable from 9-AA by copolymerization with 1-NA if the feed ratio of 9-AA to 1-NA is less than 1.

Electronic absorption spectra of the polymers indicate that poly(1-AA) has an absorption maximum at a very long wavelength region (570 nm), which is 60 nm longer than poly(1-NA) (Fig. 1). The cutoff wavelength of poly(1-AA) reached 760 nm. This is a clear indication of extremely wide conjugation of the main chain. The copolymer of 9-AA with 1-NA also exhibits a red-shifted absorption maximum at 530 nm (Fig. 2). The long cutoff wavelength of this copolymer ( $> 700$  nm) contributes to the large magnitude of the third-order nonlinear optical susceptibility [ $\chi^{(3)}(-3\omega; \omega, \omega, \omega) = 40 \times 10^{12}$  esu] (Table 2). In contrast, poly(2-AA) shows no absorption maximum, and a cutoff wavelength is observed below 700 nm.

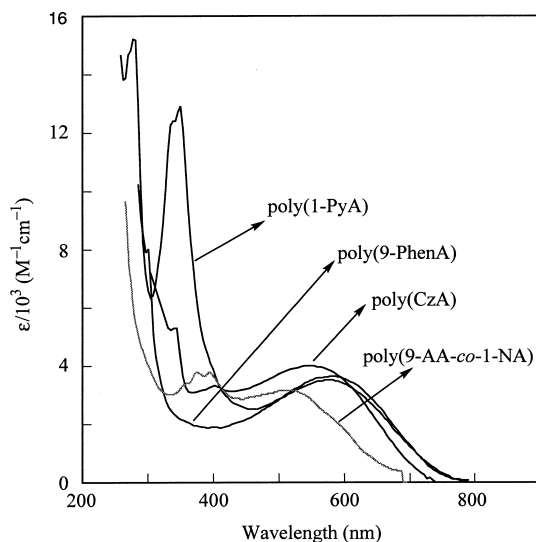


Fig. 2. UV-vis spectra of poly(9-PhenA), poly(1-PyA), poly(CzA), and poly(9-AA-*co*-1-NA) in chloroform.

### 2.3. Phenanthrylacetylenes

2- and 3-Phenanthrylacetylenes (2-PhenA and 3-PhenA, respectively) polymerize with  $WCl_6$ -based catalysts, resulting in the formation of dark brown to purple polymers in moderate yields [10]. The molecular weights of these polymers are 10,000–24,000, and both poly(2-PhenA) and poly(3-PhenA) are soluble in common solvents. No polymers are obtained with Mo catalysts. On the other hand, 9-phenanthrylacetylene (9-PhenA) gave partly soluble polymers with deep color (dark purple), which indicates wider main-chain conjugation of poly(9-PhenA) than those of poly(2-PhenA) or poly(3-PhenA) [12]. The molecular weight of poly(9-PhenA) remains not more than 10,000, which is probably due to the insolubility of the polymer in polymerization solvent (toluene). However, introduction of aliphatic pendants onto the phenanthryl group enables to afford a soluble poly(9-PhenA). For example, Yamaguchi et al. succeeded in the formation of a soluble polymer ( $M_n = 20,000$ ) from 3,6-dibutyl-9-phenanthrylacetylene (9-PhenA-Bu<sub>2</sub>) with **1** [14].

Resulting from the polymer colors, UV–vis spectra of the polymers show a drastic difference in the cutoff wavelength between phenanthrylacetylenes. For example, poly(2-PhenA) and poly(3-PhenA) exhibit cutoff wavelengths around 700 nm, whereas that of poly(9-PhenA) reaches 800 nm (Fig. 2). Introduction of alkyl chain to the polymer, i.e., poly(9-PhenA-Bu<sub>2</sub>), is likely to narrow the main-chain conjugation since the wavelength of the absorption maximum of poly(9-PhenA-Bu<sub>2</sub>) is shorter than that of the parent poly(9-PhenA).

### 2.4. Other arylacetylenes

1-Pyrenylacetylene (1-PyA) also undergoes polymerization with W catalyst to give a partly soluble polymer in good yield [12]. The  $M_n$  of the polymer is between 2000 and 6000. The use of Mo and Rh catalysts leads to the formation of

insoluble materials in low yield. Poly(1-PyA)s obtained with W catalysts are deeply colored (dark purple), and those with Mo catalysts are reddish brown. The UV–vis spectrum of the soluble part of poly(1-PyA) shows an absorption maximum at 580 nm (Fig. 2). The cutoff wavelength is observed at 800 nm, which is approximately 90 and 20 nm longer than those of poly(3-PhenA) and poly(1-AA), respectively. A widely conjugated polymer with good solubility is also attainable from a heteroatom-containing monosubstituted acetylene. Namely, *N*-carbazolylacetylene (CzA) smoothly polymerizes with  $WCl_6$ -based catalysts to a dark purple polymer with excellent solubility in common solvents [17]. Poly(CzA) presents absorption maximum and cutoff wavelength at 550 and 740 nm, respectively (Fig. 2).

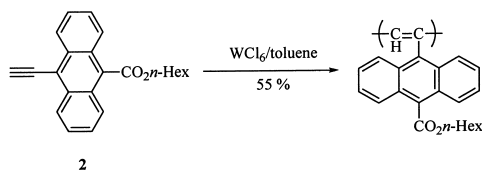
## 3. Discussion

From the above-stated results, the following tendencies can be recognized. First, W catalysts are advantageous for the production of polymers in high yield. All the polymers presented in this article are obtainable in satisfactory yields with W catalysts and they are partly or completely soluble in chloroform. On the other hand, Mo and Rh catalysts often fail in the formation of polymers, or produce insoluble materials in poor yields. Second, judging from the color of the polymer, W catalysts provide higher extent of main-chain conjugation than Mo catalysts. In other words, *trans*-rich polymers possess wide main-chain conjugation. This is in good agreement with the fact that helical main-chain conformation is readily attainable from the *cis*-rich polyacetylenes [8]. Thirdly, increase in the steric hindrance between the main chain and the pendant groups tends to enhance the main-chain conjugation. For example, 2-AA and 2-PhenA, whose unsubstituted aromatic rings direct to the opposite site to the triple bond, give polymers with bright color, and no absorption maximum peak is detected in UV–vis region for these

polymers. On the contrary, poly(1-AA) and poly(9-PhenA), which have a large repulsion between the unsubstituted aromatic rings and the main chain, are deeply colored and exhibit red-shifted absorption above 560 nm (Fig. 1). In these cases, the large steric hindrance also exists between the pendant groups, which forces the aromatic rings to twist out of the backbone plane. Due to the planar structure of the aromatic rings, the repulsion between the pendant groups is eventually reduced, which allows the main chain to exist in nearly planar conformation.

Although the above strategy can offer acetylene-based widely conjugated polymers, there are still several problems to be solved. For example, most of the widely conjugated polymers having absorption maxima above 560 nm [poly(1-AA), poly(9-PhenA) and poly(1-PyA)] are only partly soluble in common organic solvents. Poly(1-AA) only slightly dissolves even in *o*-dichlorobenzene, which is known as a good solvent for polymers with low solubility such as polyethylene. Therefore, most of the polymerizations proceed heterogeneously. Furthermore, the molecular weights of the polymers are unsatisfactory, due in part to poor solubility. Even the soluble polymer, poly(9-PhenA-Bu<sub>2</sub>), shows a moderate molecular weight of 20,000. Eventually, self-standing films cannot be obtained from these polymers, and the stability of the polymers in solution cannot be estimated<sup>3</sup>. These problems, which have been combined with the abovementioned strategy, stimulated us to design a new substituted acetylene, **2**, with the motivation of synthesizing soluble and stable polymers with high order of main-chain conjugation (Scheme 2) [20].

Design of **2** is based on the following guideline. First, a long alkyl chain should be incorporated onto the condensed aromatic rings to enhance the polymer solubility. Second, electron-withdrawing groups that reduce the electron



Scheme 2.

density of the main chain should be introduced to improve the stability of the main chain against oxidative cleavage [21]. Finally, in order to increase the steric hindrance between the main chain and pendant groups, poly(9-AA) was selected as a basic polymer skeleton. A new anthrylacetylene, **2**, was prepared by the carboxylation of commercially available inexpensive 9,10-dibromoanthracene, the esterification of the carboxyl group via the carbonyl chloride, the Pd-catalyzed Sonogashira coupling with trimethylsilylacetylene, followed by the desilylation with tetrabutylammonium fluoride. The monomer **2** has been proven to smoothly polymerize with WCl<sub>6</sub> to a high molecular weight polymer ( $M_n = 171 \times 10^3$ ) [20]. It should be noted that the polymerization system is completely homogeneous. Poly(**2**) is a deeply colored solid (almost black in the solid state), and readily soluble in common solvents such as THF, chloroform and toluene. Resulting from its high molecular weight, poly(**2**) has good film-forming ability; casting the chloroform solution of poly(**2**) gives a freestanding film. Poly(**2**) shows absorption maximum and cutoff wavelength at 571 and 780 nm, respectively, indicating a very high order of main-chain conjugation. It is noteworthy that poly(**2**) is much more stable in solution than poly(phenylacetylene). For example, whereas poly(phenylacetylene) rapidly degrades into oligomers within few hours in chloroform, poly(**2**) retains its molecular weight under the same conditions.

#### 4. Summary

The past observation that the polymers from monosubstituted acetylenes are generally unsta-

<sup>3</sup> For the degradation of poly(phenylacetylene), see Refs. [18,19].

ble and possess low degrees of conjugation reminds us that they are essentially impossible to be applied as functional materials based on the main-chain  $\pi$ -conjugation. However, the systematic efforts have broken this spell. An appropriate design of monomer enables to supply highly conjugated substituted polyacetylenes with excellent processability, solubility, and stability. We believe that the concept demonstrated here will provide a route to a polyacetylene-based new material with unexpected functionalities.

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