# Metathesis Polymerization of 9-(10-Hexoxycarbonyl)anthrylacetylene. A Route to a Widely Conjugated Polyacetylene with Excellent Stability and Solubility

**Ryoji Nomura,[†] S. M. Abdul Karim,[†] Hirotake Kajii,[‡] Rahmat Hidayat,[‡] Katsumi Yoshino,[‡] and Toshio Masuda*[,†]**

*Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan, and Department of Electronic Engineering, Faculty of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan*

*Received February 29, 2000*

The most widely conjugated synthetic polymer is undoubtedly represented by polyacetylene which exhibits metallic conductivity upon doping.[1] Its instability and insolubility, however, essentially inhibit practical application to functional materials. An elegant approach to stable and soluble substituted polyacetylenes with high order of conjugation is the cyclopolymerization of 1,6-heptadiynes with substituents.[2] The presence of cyclic structure allows the polymer backbones to exist in nearly coplanar conformation, which contributes to their characteristic properties as highly conjugated polymers. In contrast, the polymerization of monosubstituted acetylenes has been regarded as an ineffective route to widely conjugated acetylenic polymers because the coplanarity of the main chain is hampered by the steric hindrance between the substituents.[3]

However, our recent studies on the polymerization of a wide variety of arylacetylenes have led to a conclusion that polymers with considerably wide conjugation along the main chain are accessible from monosubstituted acetylenes bearing bulky but planar substituents.[4] Namely, acetylenes with condensed aromatic rings, which directly attach to the C−C triple bond in such a way to increase the steric hindrance between the main chain and pendant group, give widely conjugated polymers in the presence of W catalysts.[4] It is unfortunate, however, insufficient solubility of most of these polymers prevents the formation of high molecular weight polymers with processability such as film-forming ability.[5] Furthermore, the stability of these polymers in solution cannot be estimated due to the poor solubility notwithstanding the plausible degradation of the polymers from monosubstituted actylenes.[6]

This background stimulated us to design a new acetylenic monomer, 9-(10-hexoxycarbonylanthrylacetylene), **1** (Scheme 1), with the motivation of producing an acetylene-based widely conjugated polymer having excellent solubility and stability as well as high molecular weight. The design of **1** is based on the following strategies. First, an alkyl chain should be incorporated to the condensed aromatic ring to improve the solubility. Second, to enhance the film-forming ability, a polar substituent that does not deactivate the W catalysts should be introduced. Finally, poly(anthrylacetylene),[4b] which possesses a large steric hindrance between the pendant and the main chain, should be selected as the basic polymer skeleton.

The synthesis of **1** was performed as outlined in Scheme 1. Commercially available and inexpensive 9,10-dibromoanthracene was transformed into the corresponding monocarboxylic acid, which was converted into the haloester via the acid chloride.[7] An attempt to directly transform the carboxylic acid into the ester in the presence of an acid catalyst failed owing to the steric hindrance of the anthracene ring. The Sonogashira coupling[8] of the haloester with trimethylsilylacetylene successfully gave the coupled product although a prolonged reaction period was required (3 days at room temperature), where even the use of THF as solvent in the coupling reaction[9] did not accelerate the reaction. Desilylation with tetrabutylammonium fluoride gave **1** in 46% total yield. Oligomerization of **1** was unavoidable when the desilylation was conducted under alkaline conditions by using NaOH in methanol.

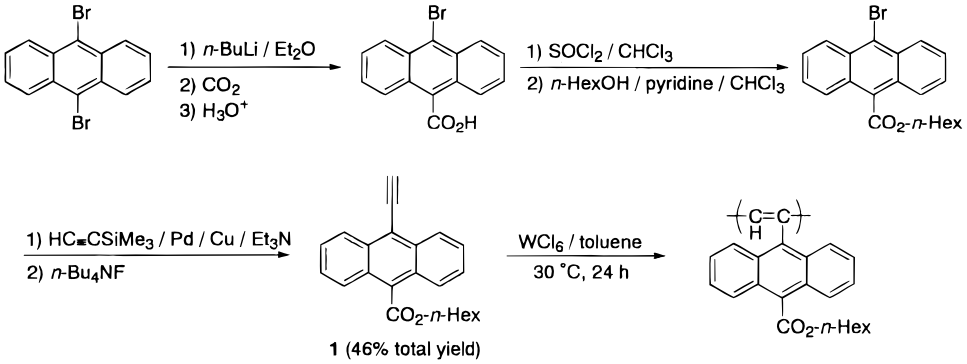
$WCl_6$-catalyzed polymerization of **1**[10] gave a deeply colored polymer (almost black in the solid state, 55% yield) that was readily soluble in common solvents such as THF, $CHCl_3$, toluene, and so forth. At least 30 mg of poly(**1**) completely dissolved in 1 mL of toluene or THF. This high solubility of poly(**1**) is contrastive to the lack of solubility of its parent polymer, poly(9-anthrylacetylene).[4b] The IR spectrum of poly(**1**) showed no absorption due to the C−H stretching and bending vibrations of the acetylene group which were clearly observed in the IR spectrum of **1** at 3258 and 661 $cm^{-1}$, respectively. The signal attributed to the acetylenic proton of **1** at 4.04 ppm disappeared after the polymerization, and the $^1H$ NMR spectrum of poly(**1**) gave very broad signals in the region of aromatic and olefinic protons. These suggest that the acetylene triple bonds have been transformed to the olefin double bonds by the polymerization and that a polymer with trans-rich stereostructure was formed. Gel permeation chromatographic analysis of poly(**1**) (eluent, $CHCl_3$; PSt calibration) indicated the formation of a high molecular weight polymer ($M_n = 1.71 \times 10^5$, $M_w/M_n = 2.1$). The absolute molecular weight of poly(**1**) is probably higher than the estimated one because GPC analyses tend to underestimate the molecular weight of several living polymers from substituted acetylenes.[11] Thanks to the high molecular weight and the presence of polar functional groups, poly(**1**) is feasible to give a free-standing film by casting a THF solution.

The UV−vis spectrum of poly(**1**) showed an absorption maximum and cutoff at 571 and 780 nm, respectively (Figure 1). Because no absorption was observed in this region in the UV−vis spectrum of monomer **1**, the red-shifted absorption is attributed to the electronic transitions of the main-chain chromophores. Thus, the observed absorption results from the conjugation along the backbone of poly(**1**). The extremely wide conjugation of poly(**1**) is readily recognized by the comparison of the UV−vis spectrum of poly(**1**) with that of poly(phenylacetylene). This wide main-chain conjugation is contrastive to the low extent of the main-chain conjugation of poly(2-anthrylacetylene), a geometrical isomer of poly(**1**), which shows a cutoff at 700 nm and no absorption maximum.[4c] Therefore, the substitution position plays a very important role for the formation of widely

[†] Kyoto University.
[‡] Osaka University.
* Corresponding author. Tel +81-75-753-5613; Fax +81-75-753-5908; E-mail masuda@adv.polym.kyoto-u.ac.jp.

10.1021/ma0003708 CCC: $19.00 
Published on Web 05/24/2000

**Scheme 1**



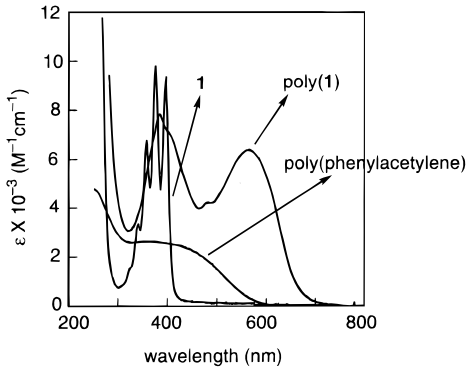
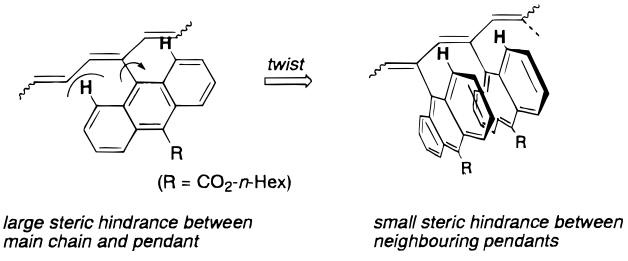




**Figure 1.** UV−vis spectra of monomer **1**, poly(**1**), and poly(phenylacetylene) in $CHCl_3$.

**Scheme 2**




conjugated polymers from monosubstituted arylacetylenes. The large steric hindrance between the polymer backbone and the protons at 1 and 8 positions probably renders the anthryl rings to twist out of the backbone. This hypothesis is supported by a simple molecular orbital calculation (PM3) of the corresponding unimers, 9- and 2-vinylanthracene: the dihedral angle between the vinyl and anthryl ring was estimated to be 80.8° and 0.2° for the most stable conformations of 9-vinylanthracene and 2-vinylanthracene, respectively. This result clearly demonstrates ineffective conjugation between the main chain and pendant group in poly(**1**). The twist of the anthryl ring of poly(**1**), on the other hand, yields no significant steric repulsion between neighboring pendant groups because of the planar structure of the anthryl group. This reduced steric interaction between pendants probably allows the polymer backbone to exist in a coplanar conformation (Scheme 2), which explains the expanded conjugation along the polymer backbone.

The wide conjugation along the main chain led to a very large magnitude of the third-order nonlinear optical (NLO) susceptibility of poly(**1**); i.e., the real part of $\chi^{(3)}(-\omega;\ \omega,0,0)$ was $-1.9 \times 10^{-10}$ esu (631 nm) determined by the electroabsorption measurement, which is 1 order larger than those of ortho-substituted poly(phenylacetylene)s.[12] The electrical conductivity of poly(**1**), measured by a conventional two-probed technique employing Keithley's electrometer in a vacuum, was $8.77 \times 10^{-4}$ and $2.60 \times 10^{-15}$ S/cm at the $I_2$-doped and undoped states.

Poly(**1**) was thermally very stable in the solid state. No weight loss was detected below 300 °C by thermogravimetric analyses (TGA) in nitrogen, and 5% weight loss was observed at 350 °C. The TGA displayed two stages on weight loss of poly(**1**); the first weight loss left ca. 60% of weight residue below 490 °C, which agreed well with the predicted value assuming that the pendant ester group was lost first upon heating. Emphasis should be placed on the stability of **1** in solution. Most of the polymers from monosubstituted arylacetylenes decompose into oligomers in solution,[6b,c] and the degradation is extremely rapid in chloroform. For example, poly(phenylacetylene) with $M_n$ of $2.25 \times 10^5$ degraded into oligomers ($M_n$ = 9000) within 4 h in chloroform. Introduction of ester groups to poly(phenylacetylene) can reduce the electron density of the main chain, which retarded the degradation. Degradation of poly(*p*-methoxycarbonylphenylacetylene) into oligomers, however, was also unavoidable, where the initial value of $M_n$ ($2.87 \times 10^5$) decreased to $2.40 \times 10^4$ after 12 h in chloroform. In contrast, the degradation of poly(**1**) was much slower than that of poly(*p*-methoxycarbonylphenylacetylene), and poly(**1**) with initial $M_n$ of $1.71 \times 10^5$ maintained relatively high molecular weight ($M_n$ = $1.06 \times 10^5$) even after the treatment in chloroform for 24 h. Thus, the bulky condensed aromatic ring contributes to the stabilization of the polymer main chain against the degradation.

**Acknowledgment.** The authors are grateful to Professor T. Wada and Professor H. Sasabe for the measurement of NLO. We are also indebted to Dr. T. Kobatake for the measurement of the mass spectrum. This research was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science, Culture, and Sports, Japan.

**Supporting Information Available:** Detailed experimental procedures for the synthesis of the monomer. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) For reviews of the synthesis and properties of polyacetylene, see: (a) Curran, S.; Starhauser, A.; Roth, S. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: Chichester, 1997; Vol. 2, p 1. (b) Shirakawa,

H.; Masuda, T.; Takeda, K. In *The Chemistry of Triple-Bonded Functional Groups (Supplement C2)*; Patai, S., Ed.; Wiley: Chichester, 1994; p 945. (c) Chien, J. C. W. *Polyacetylene*; Academic Press: New York, 1984.

(2) For a review of the polymerization of 1,6-heptadiynes with substituents, see: Choi, S. K.; Lee, J. H.; Kang, S. J.; Jin, S. H. *Prog. Polym. Sci.* **1997**, *22*, 693−734. See also ref 3.

(3) For reviews of transition-metal-catalyzed polymerization of substituted acetylenes, see: (a) Masuda, T. In *Catalysis in Precision Polymerization*; Kobayashi, S., Ed.; Wiley: Chichester, 1997; Chapter 2.4. (b) Masuda, T. In *Polymeric Material Encyclopedia*; Salamone, J. C., Ed.; CRC: New York, 1996; Vol. 1, p 32.

(4) (a) Karim, S. M. A.; Musikabhumma, K.; Nomura, R.; Masuda, T. *Proc. Jpn. Acad. Ser. B* **1999**, *75*, 97−100. (b) Nanjo, K.; Karim, S. M. A.; Nomura, R.; Wada, T.; Masuda, T. *J. Polym. Sci., Polym. Chem.* **1999**, *37*, 277−282. (c) Musikabhumma, K.; Masuda, T. *J. Polym. Sci., Polym. Chem.* **1998**, *36*, 3131−3137.

(5) Only one example has been communicated for the synthesis of a soluble polymer from 9-phenanthrylacetylene having aliphatic pendant groups. The stability of this polymer has not been evaluated. See: Yamaguchi, M.; Hirama, M.; Nishihara, H. *Chem. Lett.* **1992**, 1667−1668.

(6) For degradation of polyacetylenes, see: (a) Masuda, T.; Tang, B.-Z.; Higashimura, T.; Yamaoka, H. *Macromolecules* **1985**, *18*, 2369−2373. (b) Vohlidal, J.; Rédrová, D.; Pacovská, M.; Sedlácek, J. *Collect. Czech. Chem. Commun.* **1993**, *58*, 2651−2662. (c) Sedlácek, J.; Vohlidal, J. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 51−53.

(7) Bayliss, M. A. J.; Homer, R. B.; Shepherd, M. J. *J. Chromatogr.* **1998**, *445*, 393−402.

(8) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−630.

(9) Thorand, S.; Krause, N. *J. Org. Chem.* **1998**, *63*, 8551−8553.

(10) The polymerization was conducted as follows. A toluene solution of **1** and $WCl_6$ was kept for 24 h at 30 °C in a Schlenk tube under nitrogen. The concentrations of the monomer and catalyst were 200 and 10 mM, respectively. The resulting viscous solution was diluted in toluene and then poured into a large amount of methanol. Filtration followed by drying under reduced pressure gave poly(**1**) as a black powder in 55% yield.

(11) The following relationship has been obtained for poly[*o*-(trifluoromethyl)phenylacetylene]: $M_n$(VPO) = 1.48$M_n$-(GPC). See: Kaneshiro, H.; Hayano, S.; Masuda, T. *Macromol. Chem. Phys.* **1999**, *200*, 113−117.

(12) Wada, T.; Masuda, T.; Sasabe, H. *Mol. Cryst. Liq. Cryst.* **1994**, *247*, 139−147.

MA0003708