Journal of Materials Science and Engineering B 3 (7) (2013) 423-430

Transition-Metal-Catalyzed Highly Regio- and Stereoselective Co-Polymerization of Dialkynylbenzene with Benzenedithiol Leading to Poly(Phenylene Vinylene Sulfide)

Takuma Ikeda[1], Naoki Nakagawa[1], Akihiro Nomoto[1], Yuta Minatobe[1], Shin-ichi Fukuzawa[3], Toshikazu Hirao[2] and Akiya Ogawa[1]

1. Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Nakaku, Sakai, Osaka 599-8531, Japan

2. Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

3. Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, Bunkyo-ku, Tokyo 112-8551, Japan

Received: May 25, 2013 / Accepted: June 20, 2013 / Published: July 25, 2013.

Abstract: Co-polymerization of dialkynylbenzene with benzenedithiol proceeds regio- and stereoselectively in the presence of transition metal catalysts, affording the corresponding poly(phenylene vinylene sulfide) in good yield. In the presence of palladium acetate as catalyst, Markovnikov addition takes place selectively, whereas chlorotris(triphenylphosphine)rhodium-catalyzed reaction affords anti-Markovnikov adduct with excellent regio- and stereoselectivity.

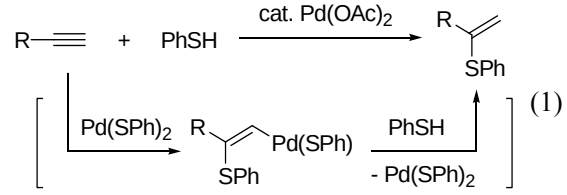
Key words: Poly(phenylene vinylene sulfide), transition-metal-catalyzed reaction, stereoselective reaction, regioselective reaction, Markovnikov addition.

1. Introduction

Poly(phenylene), poly(vinylene), poly(phenylene vinylene), and poly(phenylene sulfide) are among representative π-conjugated polymers and their electrical conductivity has been focused recently. To control the chemical or electrical properties of polymer, the development of highly selective synthetic methods of them is of great importance [1-9]. Transition-metal-catalyzed co-polymerization methods are one of the most suitable candidate for highly selective synthesis of π-conjugate polymers, and indeed poly(phenylene) and poly(phenylene vinylene) can be prepared by this method [10-15]. However, the examples of the transition-metal-catalyzed synthesis of poly(phenylene sulfide) and poly(phenylene vinylene sulfide) has been largely unexplored [16-28], most probably because organosulfur compounds are wide-spread believed to be catalyst poisons [29]. Recently, we have developed a series of highly selective transition-metal-catalyzed reactions of organosulfur compounds with acetylenes [30-33], and therefore this prompted us to examine the construction of π-conjugated system.

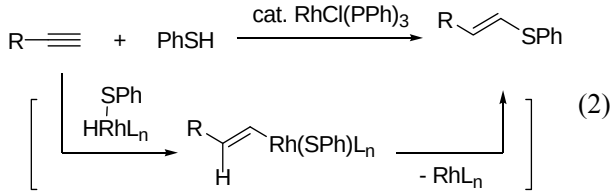
In our previous paper, we have revealed that the palladium acetate catalyzes the Markovnikov addition of thiols to terminal alkynes (Scheme 1) [30]. The reaction may proceed via the formation of palladium sulfide ($Pd(SPh)_2$), followed by thiopalladation of alkynes and protonolysis of thus formed vinylpalladium species with thiol.

Corresponding author: Akihiro Nomoto, Ph.D., Lecturer, research fields: organic synthesis, materials science and metal complexes., E-mail: nomoto@chem.osakafu-u.ac.jp.



(1)

On the other hand, changing the catalyst from palladium acetate to Wilkinson's catalyst ($RhCl(PPh_3)_3$) causes anti-Markovnikov addition of thiols to terminal alkynes with excellent stereoselectivity (*syn*-addition) (Scheme 2) [31]. The reaction may involve the oxidative addition of thiols to the catalyst generating $HRh(SPh)Cl(PPh_3)_3$, followed by hydrorhodation of alkynes and reductive elimination of the product with recovery of the catalyst.



(2)

In this paper, regio- and stereoselectivities were described on transition-metal-catalyzed addition reactions of thiols to alkynes, and this synthetic methodology was also applied to co-polymerization of dialkynylbenzene with benzenedithiol leading to poly(phenylene vinylene sulfide).

2. Experiments

2.1 Instrumentation

^{1}H-NMR spectra were recorded on a JEOL JNM-AL-300 or JEOL JNM-AL-400 spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard. Chemical shifts in ^{13}C-NMR were measured relative to $CDCl_3$ by using δ 77.0 ppm. IR spectra were determined on a Shimadzu FTIR 8400 infrared spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus. Mass spectra were obtained on a JEOL JMS-DX303 in the analytical section of Osaka University. Elemental analyses were also performed there. All materials were obtained from commercial supplies and purified by distillation or recrystallization. Molecular weights and molecular weight distributions of polymers were determined with a Shodex-KF804 (Showa Denko K.K.) equipped with the RI-2031 from JASCO Ltd.

2.2 p-Bis[α-(Phenylthio)Ethenyl]Benzene 3b

For the $Pd(OAc)_2$-catalyzed hydrothiolation of *p*-diethynylbenzene (1a) with benzenethiol (2b): In a two-necked glass flask under N_2 atmosphere were placed $Pd(OAc)_2$ (5 mol%), THF (5 mL), *p*-diethynylbenzene (1a, 1 mmol), and then benzenethiol (2b, 2 mmol). The resulting mixture was stirred magnetically for 16 h with heating at 40 °C. After the reaction was complete, the reaction mixture was filtered through Celite, followed by washing with diethyl ether. The combined filtrate was concentrated under the reduced pressure. The purification by preparative TLC on silica gel using hexane:AcOEt = 100:0 to 96:4 as an eluent afforded 0.22 g (63%) of *p*-bis[α-(phenylthio)ethenyl]benzene (3b) as a colorless solid: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.29 (s, 2 H), 5.66 (s, 2 H), 7.13-7.39 (m, 14 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 116.2, 127.1, 127.3, 129.1, 131.8, 133.6, 138.8, 143.8; IR (KBr) 3,054, 1,582, 1,474, 1,436, 1,394, 1,273, 1,070, 846, 744, 688 cm^{-1}; Anal. Calcd for $C_{22}H_{18}S_2$: C, 76.26; H, 5.24. Found: C, 76.53; H, 5.30.

2.3 m-Bis(α-Styrylthio)Benzene 3c

For the $Pd(OAc)_2$-catalyzed hydrothiolation of phenylacetylene (1b) with benzenedithiol (2a): In a two-necked glass flask under N_2 atmosphere were placed $Pd(OAc)_2$ (5 mol%), THF (5 mL), phenylacetylene (1b, 2 mmol), and then benzenedithiol (2a, 1 mmol). The resulting mixture was stirred magnetically for 16 h with heating at 40 °C. After the reaction was complete, the reaction mixture was filtered through Celite, followed by washing with diethyl ether. The combined filtrate was concentrated under the reduced pressure. The purification by preparative TLC on silica gel using

hexane: AcOEt = 100:0 to 96:4 as an eluent afforded 0.21 g (60%) of *m*-bis(α-styrylthio)benzene (3c) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (s, 2 H), 5.60 (s, 2 H), 7.09-7.37 (m, 14 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.8, 127.2, 128.3, 128.5, 129.5, 130.3, 134.6, 135.0, 138.5, 143.8; IR (KBr) 3,056, 1,570, 1,487, 1,452, 1,392, 1,223, 1,071, 905, 772, 694 cm^{-1}.

2.4 p-Bis[β-(Phenylthio)Ethenyl]Benzene 6b

For the $RhCl(PPh_3)_3$-catalyzed hydrothiolation of *p*-diethynylbenzene (1a) with benzenthiol (2b): In a two-necked glass flask under N_2 atmosphere were placed $RhCl(PPh_3)_3$ (5 mol%), CH_2Cl_2 (5 mL), *p*-diethynylbenzene (1a, 1 mmol), and then benzenethiol (2b, 2 mmol). The resulting mixture was stirred magnetically for 20 h with heating at 40 ºC. After the reaction was complete, the reaction mixture was filtered through Silica short column, followed by washing with chloroform. The combined filtrate was concentrated under the reduced pressure. Recrystallization was carried out from chloroform affording 0.25 g (72%) of *p*-bis[β-(phenylthio)ethenyl]benzene (6b) as an pale yellow solid: a pale yellow solid; mp 140-144 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (d, *J* = 15.6 Hz, 2 H), 6.88 (d, *J* = 15.6 Hz, 2 H), 7.35-7.43 (m, 14 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.73, 123.77, 126.45, 127.20, 129.34, 130.12, 131.15, 135.21, 135.91; IR (KBr) 691, 735, 793, 953, 1,022, 1,070, 1,437, 1,474, 1,580, 3,018, 3,047 cm^{-1}; MS (FAB), *m/z* = 347 ($M + H^+$).

2.5 m-Bis(β-Styrylthio)Benzene 6c

For the $RhCl(PPh_3)_3$-catalyzed hydrothiolation of phenylacetylene (1b) with benzenedithiol (2a): In a two-necked glass flask under N_2 atmosphere were placed $RhCl(PPh_3)_3$ (5 mol%), CH_2Cl_2 (5 mL), phenylacetylene (1b, 2 mmol), and then benzenedithiol (2a, 1 mmol). The resulting mixture was stirred magnetically for 20 h with heating at 40 ºC. After the reaction was complete, the reaction mixture was filtered through Silica short column, followed by washing chloroform. The combined filtrate was concentrated under the reduced pressure affordeding 0.25 g (72%) of *m*-bis(β-styrylthio)benzene (6c) as a brown solid: a brown solid; mp 98-101 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 15.2 Hz 2 H), 6.87 (d, *J* = 15.6 Hz, 2 H), 7,24-7.36 (m, 14 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 122.4, 126.4, 127.9, 128.1, 128.9, 129.9, 133.3, 136.6, 137.2; IR (KBr) 691, 743, 775, 955, 1,084, 1,232, 1,394, 1,462, 1,485, 1,558, 1,568 cm^{-1}; MS (FAB), *m/z* = 347 ($M+H^+$).

2.6 1,4-Bis[β-(Phenylthio)Pentenyl]Benzene 7b

Yellow oil, 0.34 g (78%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 6 H), 1.64 (sextet, *J* = 7.5 Hz, 4 H), 2.41 (t, *J* = 8.1 Hz, 4 H), 6.69 (s, 2 H), 7.21-7.39 (m, 14 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.2, 33.7, 126.8, 128.26, 128.30, 132.0, 132.1, 133.4, 136.8, 138.8; IR (NaCl) 3,056, 2,959, 2,869, 1,610, 1,573, 1,472, 1,098, 1,014, 818, 746, 697 cm^{-1}; MS (EI), *m/z* = 430 (M^+, 100.0). Anal. Calcd for $C_{28}H_{30}S_2$: C, 78.09; H, 7.02. Found: C, 78.08; H, 7.13.

2.7 1,4-Bis[2'-(1'-Phenyl-Pent-1'-Enyl)Thio]Benzene 7c

Yellow oil, 0.36 g (84%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.5 Hz, 6 H), 1.61 (sextet, *J* = 7.8 Hz, 4 H), 2.35 (t, *J* = 8.1 Hz, 4 H), 6.51 (s, 2 H), 7.12-7.39 (m, 14 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.2, 33.8, 127.3, 128.3, 129.0, 130.4, 132.0, 134.0, 135.4, 139.7; IR (NaCl) 3,071, 2,958, 2,869, 1,609, 1,582, 1,475, 1,439, 1,124, 1,024, 887, 743, 691 cm^{-1}; MS (EI), *m/z* = 430 (M^+, 100.0). Anal. Calcd for $C_{28}H_{30}S_2$: C, 78.09; H, 7.02; S, 14.89. Found: C, 77.75; H, 6.84; S, 14.51.

2.8 Poly(Phenylene Vinylene Sulfide) 3a and 6a

In a two-necked glass flask under N_2 atmosphere were placed catalyst (5 mol%), CH_2Cl_2 (5 mL), *p*-diethynylbenzene (1a, 1 mmol), and then

benzenedithiol (2a, 1 mmol). The resulting mixture was stirred magnetically for 20 h with heating at 40 °C. Precipitates were formed. The reaction mixture was filtered, and solid was collected without further purification.

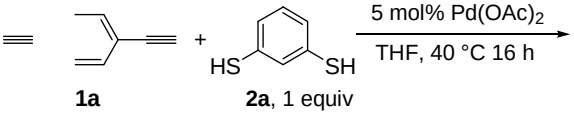
3a: reddish brown solid, 0.11 g (41%); IR (KBr) 3,050, 1,563, 1,500, 1,457, 1,392, 1,258, 1,060, 772, 680 cm^{-1}. 6a: reddish brown solid, 0.15 g (55%); IR (KBr) 3,010, 1,567, 1,500, 1,458, 1,394, 1,099, 941, 772, 682 cm^{-1}.

2.9 Poly(Phenylene Vinylene Sulfide) 7a

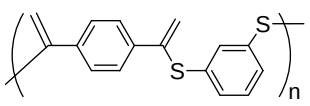
In a two-necked glass flask under N_2 atmosphere were placed $RhCl(PPh_3)_3$ (15 mol%), CH_2Cl_2 (5 mL), *p*-bis(1-pentynyl)benzene (1c, 1 mmol) and then *p*-benzendithiol (2c, 1 mmol). The resulting mixture was stirred magnetically for 20 h with heating at 40 °C. After the reaction was complete, the reaction mixture was filtered through Silica short column, followed by washing with chloroform, and further purification was carried out by preparative GPC; orange powder, 0.23 g (66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz), 1.66 (sextet, *J* = 7.2 Hz), 2.42 (t, *J* = 7.2 Hz), 6.63 (s), 7.19-7.38 (m).

3. Results and Discussion

To construct sulfur-containing π-conjugated polymers, we first examined the palladium acetate-catalyzed co-polymerization of diethynylbenzene with benzenedithiol (Eq. (3)).



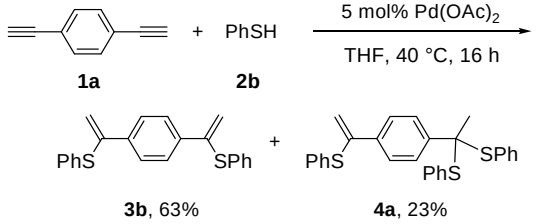
1a **2a**, 1 equiv



(3)

3a, reddish brown solid

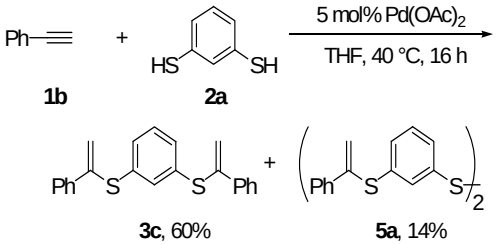
When the reaction of *p*-diethynylbenzene (1a) with equimolar amounts of *m*-benzenedithiol (2a) was conducted at 40 ºC for 16 h in the presence of palladium acetate in THF, a reddish brown solid (3a) was obtained. Since the solid was insoluble in usual solvents, the structure of the solid (3a) was assumed by comparing its IR spectrum with those of its analogues (3b and 3c), which were synthesized as shown in Eqs. (4) and (5).



1a **2b**

3b, 63% **4a**, 23%

(4)



1b **2a**

3c, 60% **5a**, 14%

(5)

The $Pd(OAc)_2$-catalyzed reaction of *p*-diethynylbenzne (1a) with benzenethiol (2b) under the identical conditions afforded *p*-bis[α-(phenylthio)ethenyl]benzene (3b) in 63% yield along with the over addition product (4a) (Eq. (4)).

Furthermore, we examined the $Pd(OAc)_2$-catalyzed reaction of phenylacetylene (1b) with *m*-benzenedithiol (2a) under identical conditions, which afforded *m*-bis(α-styrylthio)benzene (3c) in 60% yield along with bis[α-stylylthio)phenyl] disulfide (5a) (Eq. (5)). The comparison of the IR spectrum of 3a with those of 3b and 3c strongly suggests that 3a has 3b and 3c as partial structures (Fig. 1).

We next examined the $RhCl(PPh_3)_3$-catalyzed co-polymerization of *p*-diethynylbenzne (1a) with *m*-benzenedithiol (2a) in CH_2Cl_2 at 40 ºC for 20 h, which provided a yellow solid (6a) (Eq. (6)).

To get some information about the regio- and stereoselectivities of this co-polymerization, the $RhCl(PPh_3)_3$-catalyzed addition of benzenethiol (2b) to *p*-diethynylbenzne (1a) was conducted under identical conditions, and *p*-bis[β-(phenylthio)ethenyl]benzene (6b) was obtained with excellent regio- and stereoselectivities in 72% yield (Eq. (7)).

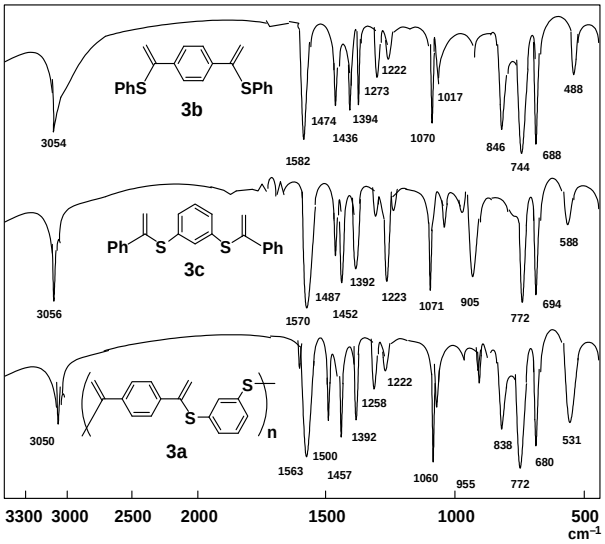
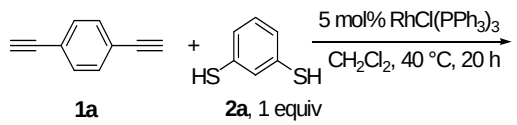
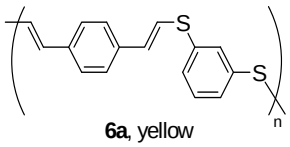
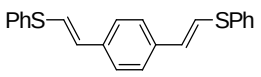


Fig. 1 IR spectra (KBr) of the adducts 3a, 3b, and 3c.

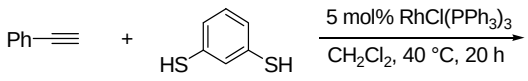


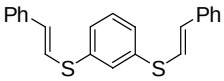


6a, yellow (6)



6b, 72% (7)



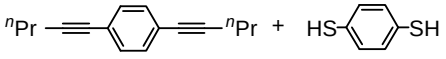


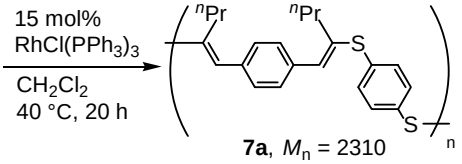
6c, 72% (8)

Similarly, the rhodium(I)-catalyzed addition of *m*-benzenedithiol (2a) to phenylacetylene (1b) took place under identical conditions to give *m*-bis(β-styrylthio)benzene (6c), regio- and stereoselectively, in 72% yield (Eq. (8)). The fact that the IR spectrum of the yellow solid (6a) is similar as those of 6b and 6c strongly suggests the excellent regio- and stereoselectivities of the present rhodium(I)-catalyzed co-polymerization.

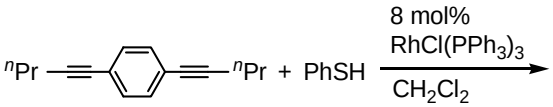
To increase the solubility of π-conjugate polymers in usual organic solvents, we next examined the synthesis of π-conjugate polymers bearing alkyl chains. When the rhodium(I)-catalyzed reaction of *p*-bis(1-pentynyl)benzene (1c) with *p*-benzendithiol (2c) was conducted in dichloromethane at 40 ºC for 20 h, poly(*p*-phenylene vinylene sulfide) derivative (7a) was obtained as a yellow solid, which was soluble in usual organic solvent (Eq. (9)).

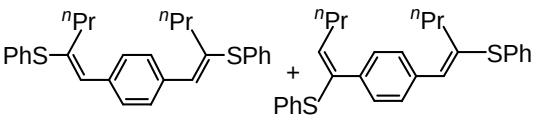
To get some information about the regio- and stereoselectivities of this rhodium(I)-catalyzed reaction using *p*-bis(1-pentynyl)benzene (1c), similar reaction of 1c with benzenethiol (2b) in the presence of $RhCl(PPh_3)_3$ was performed under identical conditions. As can be seen from Eq. (10), phenylthio group was introduced into the α-carbon of the *n*-propyl group, preferentially, with excellent stereoselectivity (*syn*-addtion). Similarly, the Rh(I)-catalyzed addition of *p*-benzendithiol (2c) to 1-phenyl-1-pentyne (1d) proceeded stereoselectively, affording the corresponding hydrothiolation product (7c), regio-preferentially (Eq. (11)).



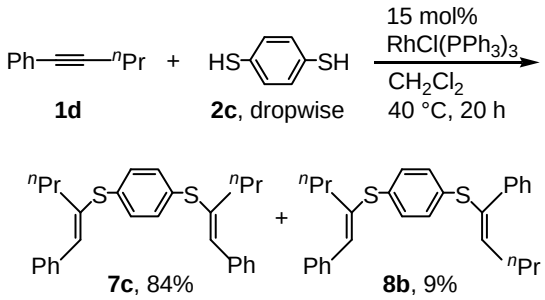


7a, M_n = 2310
M_w/M_n = 1.66 (9)





7b, 78% **8a**, 20% (10)



(11)

Fig. 2 shows the ^{1}H NMR spectrum of poly(*p*-phenylene vinylene sulfide) derivative (7a). Judging from vinylic protons, the $RhCl(PPh_3)_3$-catalyzed reaction of *p*-bis(1-pentynyl)benzene (1c) with *p*-benzendithiol (2c) proceeded with excellent regio- and stereoselectivities (only trace amounts of the regioisomer A and the stereoisomer B were obtained). This fact that the regioselectivity of the π-conjugated polymer synthesis is much higher compared with those of the reactions shown in Eqs. (10) and (11), can be explained by the bulkiness of the aryl substituenets connected directly to carbon-carbon triple bonds and sulfur atoms in the π-conjugated polymer synthesis.

Furthermore, the molecular weight (M_n) and its distribution (M_w/M_n) of the polymer (7a) were determined by the measurement using GPC (M_n = 2,310, M_w/M_n = 1.66).

4. Conclusions

Highly regio- and stereoselective syntheses of poly(phneylene vinylene sulfide) have been developed by using transition metal catalysts. We are now investigating the application of this method to the construction of some other heteroatom-containing π-conjugated systems.

Acknowledgments

This research was supported by a Grant-in-Aid for Scientific Research on Scientific Research (C, 23550057), from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by Kyoto-Advanced Nanotechnology Network.

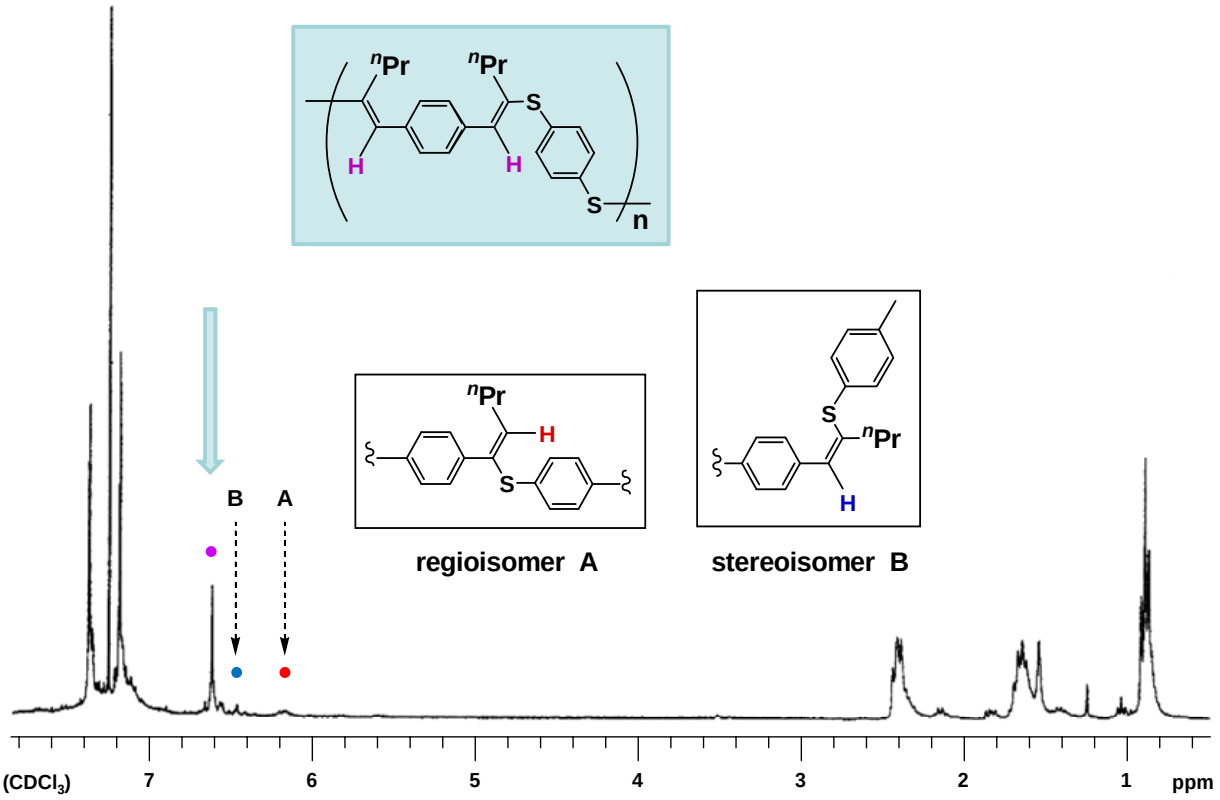


Fig. 2 ^{1}H-NMR spectra of 7a.

References

[1] W.R. Sorenson, F. Sweeny, T.W. Campbell, Preparative Methods of Polymer Chemistry, Wiley-Interscience, New York, 2001, pp. 13-40.

[2] T. Oyama, Y. Chujo, Synthesis of highly optically active polysulfoxides by asymmetric oxidation of polysulfides, Macromolecules 32 (1999) 7732-7736.

[3] F. Alonso, I.P. Beletskaya, M. Yus, Transition-metal-catalyzed addition of heteroatom-hydrogen bonds to alkynes, Chemical Reviews 104 (2004) 3079-3159.

[4] A. Kondoh, K. Takami, H. Yorimitsu, K. Oshima, Stereoselective hydrothiolation of alkynes catalyzed by cesium base: Facile access to (*Z*)-1-alkenyl sulfides, Journal of Organic Chemistry 70 (2005) 6468-6473.

[5] S. Gunes, H. Neugebauer, N.S. Sariciftci, Conjugated polymer-based organic solar cells, Chemical Reviews 107 (2007) 1324-1338.

[6] S.W. Thomas, G.D. Joly, T.M. Swager, Chemical sensors based on amplifying fluorescent conjugated polymers, Chemical Reviews 107 (2007) 1339-1386.

[7] J.Z. Liu, J.W.Y. Lam, B.Z. Tang, Acetylenic polymers: syntheses, structures, and functions, Chemical Reviews 109 (2009) 5799-5867.

[8] C.K.W. Jim, A. Qin, J.W.Y. Lam, F. Mahtab, Y. Yu, B.Z. Tang, Metal-free alkyne polyhydrothiolation: synthesis of functional poly(vinylenesulfide)s with high stereoregularity by regioselective thioclick polymerization, Advanced Functional Materials 20 (2010) 1319-1328.

[9] A. Massi, D. Nanni, Thiol-yne coupling: Revisiting old concepts as a breakthrough for up-to-date applications, Organic & Biomolecular Chemistry 10 (2012) 3791-3807.

[10] T. Yamamoto, T. Maruyama, Z.H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, et al., π-Conjugated poly(pyridine-2,5-diyl), poly(2,2'-bipyridine-5,5'-diyl), and their alkyl derivatives: Preparation, linear structure, function as a ligand to form their transition metal complexes, catalytic reactions, n-type electrically conducting properties, optical properties, and alignment on substrates, Journal of the American Chemical Society 116 (1994) 4832-4845.

[11] T. Yamamoto, Synthesis of π-conjugated polymers bearing electronic and optical functionalities by organometallic polycondensations, chemical properties and applications of the π-conjugated polymers, Synlett (2003) 425-450.

[12] S.L. Bolton, D.E. Schuehler, X. Niu, L. Gopal, M.B. Sponsler, Olefin metathesis for metal incorporation: Preparation of conjugated ruthenium-containing complexes and polymers, Journal of Organometallic Chemistry 691 (2006) 5298-5306.

[13] T. Yamamoto, T.-A. Koizumi, Synthesis of π-conjugated polymers bearing electronic and optical functionalities by organometallic polycondensations and their chemical properties, Polymer 48 (2007) 5449-5472.

[14] R. Miyakoshi, A. Yokoyama, T. Yokozawa, Development of catalyst-transfer condensation polymerization. Synthesis of pi-conjugated polymers with controlled molecular weight and low polydispersity, Journal of Polymer Science Part A: Polymer Chemistry 46 (2008) 753-765.

[15] O. Türünç, M.A.R. Meier, A novel polymerization approach via thiol-yne addition, Journal of Polymer Science Part A: Polymer Chemistry 50 (2012) 1689-1695.

[16] C.S. Cao, L.R. Fraser, J.A. Love, Rhodium-catalyzed alkyne hydrothiolation with aromatic and aliphatic thiols, Journal of the American Chemical Society 127 (2005) 17614-17615.

[17] D.A. Malyshev, N.M. Scott, N. Marion, E.D. Stevens, V.P. Ananikov, I.P. Beletskaya, et al., Homogeneous nickel catalysts for the selective transfer of a single arylthio group in the catalytic hydrothiolation of alkynes, Organometallics 25 (2006) 4462-4470.

[18] L.R. Fraser, J. Bird, Q.M. Wu, C.S. Cao, B.O. Patrick, J.A. Love, Synthesis, structure, and hydrothiolation activity of rhodium pyrazolylborate complexes, Organometallics 26 (2007) 5602-5611.

[19] A. Nakahashi, M. Fujita, E. Miyoshi, T. Umeyama, K. Naka, Y. Chujo, Synthesis of sulfur-containing hyperbranched polymers by the bisthiolation polymerization of diethynyl disulfide derivatives, Journal of Polymer Science Part A: Polymer Chemistry 45 (2007) 3580-3587.

[20] Z.C. Zhu, C.Y. Pan, A feasible synthetic route for linear PTHF-hyperbranched poly(phenyl sulfide) block copolymers, Macromolecular Chemistry and Physics 208 (2007) 1274-1282.

[21] R.L. Xu, H.W. Liu, S.Y. Liu, Y.S. Li, W.F. Shi, Effect of core structure on the fluorescence properties of hyperbranched poly(phenylene sulfide), Journal of Applied Polymer Science 107 (2008) 1857-1864.

[22] J. Yang, A. Sabarre, L.R. Fraser, B.O. Patrick, J.A. Love, Synthesis of 1,1-disubstituted alkyl vinyl sulfides via rhodium-catalyzed alkyne hydrothiolation: Scope and limitations, Journal of Organic Chemistry 74 (2009) 182-187.

[23] C.J. Weiss, S.D. Wobser, T.J. Marks, Lanthanide- and actinide-mediated terminal alkyne hydrothiolation for the catalytic synthesis of Markovnikov vinyl sulfides, Organometallics 29 (2010) 6308-6320.

[24] J.Z. Liu, J.W.Y. Lam, C.K.W. Jim, J.C.Y. Ng, J.B. Shi, H.M. Su, et al., Thiol-yne click polymerization: Regio- and stereoselective synthesis of sulfur-rich acetylenic polymers with controllable chain conformations and tunable optical properties, Macromolecules 44 (2011) 68-79.

[25] A. Di Giuseppe, R. Castarlenas, J.J. Perez-Torrente, M. Crucianelli, V. Polo, R. Sancho, et al., Ligand-controlled regioselectivity in the hydrothiolation of alkynes by rhodium n-heterocyclic carbene catalysts, Journal of the American Chemical Society 134 (2012) 8171-8183.

[26] I. Beletskaya, I. Trostyanskaya, Regio- and stereoselective copper-catalyzed addition of aromatic and aliphatic thiols to terminal and internal nonactivated alkynes, Synlett 23 (2012) 535-540.

[27] S.N. Riduan, J.Y. Ying, Y. Zhang, Carbon dioxide mediated stereoselective copper-catalyzed reductive coupling of alkynes and thiols, Organic Letters 14 (2012) 1780-1783.

[28] R. Castarlenas, A. Di Giuseppe, J.J. Perez-Torrente, L.A. Oro, The emergence of transition-metal-mediated hydrothiolation of unsaturated carbon-carbon bonds: A mechanistic outlook, Angewandte Chemie 52 (2013) 211-222.

[29] L.L. Hegedus, R.W. McCabe, Catalyst Poisoning, Marcel Dekker, New York, 1984, pp. 5-46.

[30] H. Kuniyasu, A. Ogawa, K. Sato, I. Ryu, N. Kambe, N. Sonoda, The first example of transition-metal-catalyzed addition of aromatic thiols to acetylenes, J. Am. Chem. Soc. 114 (1992) 5902-5903.

[31] A. Ogawa, T. Ikeda, K. Kimura, T. Hirao, Highly regio- and stereocontrolled synthesis of vinyl sulfides via transition-metal-catalyzed hydrothiolation of alkynes with thiols, J. Am. Chem. Soc. 121 (1999) 5108-5114.

[32] A. Ogawa, Palladium-catalyzed *syn*-addition reactions of X-Pd bonds (X = group 15, 16, and 17 elements), Handbook of Organopalladium Chemistry for Organic Synthesis John Wiley & Sons, New York, 2002, pp. 2841-2849.

[33] A. Ogawa, Selenium and Tellurium in Organic Synthesis, Wiley-VCH, Weinheim, 2004, pp. 813-866.