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Suzuki Polycondensation with a Hairpin Monomer

Yogesh Sangvikar,[†] Karl Fischer,[‡] Manfred Schmidt,[‡] A. Dieter Schlüter,[†] and Junji Sakamoto*,[†]

Laboratory of Polymer Chemistry, Department of Materials, ETH Zurich,
Wolfgang-Pauli-Strasse 10, HCI G523, CH-8093 Zurich, Switzerland, and Institute of
Physical Chemistry, Johannes Gutenberg University of Mainz, Jakob-Welder-Weg 11,
D-55099 Mainz, Germany

sakamoto@mat.ethz.ch

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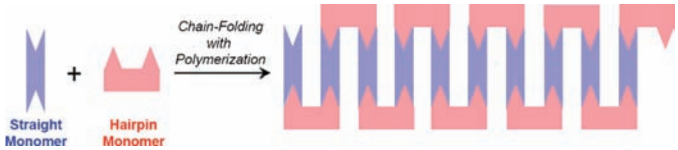
ABSTRACT



Two straight monomers were subjected to an AA/BB-type Suzuki polycondensation with a hairpin-shaped 1,8-anthrylene monomer as the counterpart leading to a novel polyarylene which should have the preferred conformation of a folded chain. The molar masses were determined by gel permeation chromatography and dynamic light scattering and found to be $M_w = 14{,}000$ and $M_n = 7{,}000$. MALDI-TOF MS analysis of a fraction provides a fingerprint of the step-growth nature of this polymerization.

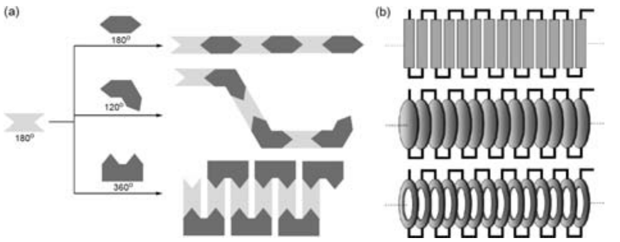


Figure 1. Impact of kinked monomers on polymer conformation (a) and possible structures formed by chain-folding with hairpin turns (b) which include ribbons (top) cylinders (medium) and tubes (bottom) depending on concrete monomer structures and intramolecular interactions such as hydrogen bonding.

The polymerization of bifunctional *p*-phenylene monomers based on successive C−C couplings leads to poly(*p*-phenylene)s. Their backbones are relatively stiff[1] and thus unlikely to fold back on themselves tightly. The rigid rodlike chains rather tend to align in a nematic or a smectic fashion.[2] Figure 1a (top) represents the copolymerization of AA- and BB-type *p*-phenylene-derived monomers, e.g., by Suzuki polycondensation (SPC).[3−5] Because of the functional groups controlling the regiochemical course of the polymerization, straight polyarylenes are the necessary product. On the other hand, if any one of the monomers is replaced by a *m*-phenylene[6] (Figure 1a, medium), the resultant polyphe-

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[†] ETH Zurich.

[‡] Johannes Gutenberg University of Mainz.

(1) Vanhee, S.; Rulkens, R.; Lehmann, U.; Rosenauer, C.; Schulze, M.; Köhler, W.; Wegner, G. *Macromolecules* **1996**, *29*, 5136.

(2) See, for example: (a) Witteler, H.; Lieser, G.; Wegner, G.; Schulze, M. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 471. (b) Harre, K.; Wegner, G. *Polymer* **2006**, *47*, 7312.

(3) For a recent comprehensive review on Suzuki−Miyaura cross-coupling, see: Miyaura, N. Metal-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2005; Vol. 1, p 41.

(4) For initial reports on rational syntheses of solubile poly(*p*-phenylene) derivatives by SPC, see: (a) Rehahn, M.; Schlüter, A. D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060. (b) Rehahn, M.; Schlüter, A. D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991.

(5) For a recent comprehensive review on SPC, see: Sakamoto, J.; Rehahn, M.; Wegner, G.; Schlüter, A. D. *Macromol. Rapid Commun.* **2009**, *30*, 653.

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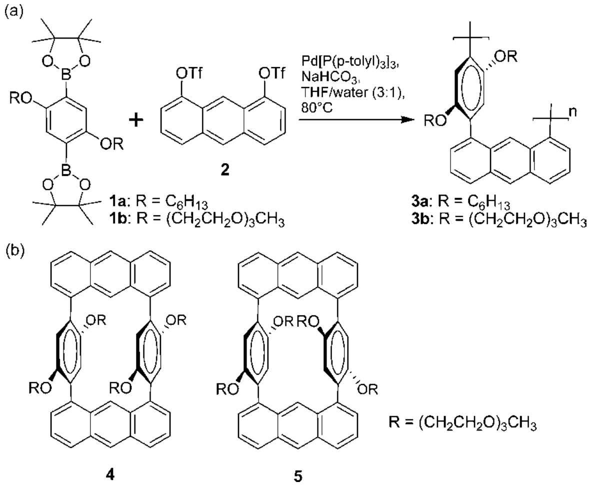
nylene is kinked so that it can attain conformations ranging from the most extended zigzag one to the more compact helical and globular ones.[7] The many conformations energetically within reach for such a polymer are considered a key factor for why a reported poly(*p*,*m*-phenylene) is amorphous in bulk and exhibits an outstanding toughness which is even comparable to that of polycarbonate.[6] Triggered by this success, we set out to further explore kinked monomers and selected a hairpin-shaped one. This forces the bond vector to periodically flip its orientation during the polymerization resulting in an enforced chain-folding (Figure 1a, bottom).[8,9] Note that this chain-folding coincides with polymerization, which is in contrast to “foldamers”, whose chain-folding is a subsequent step driven by noncovalent interactions or by changes of physical environment such as solvent polarity.[10] Depending on the particular monomer structures, the resultant polymers can not only be pseudo 2D coils[11] but also be shaped into ribbons,[12] cylinders,[13] and tubes[14] with assistance from intramolecular interactions such as hydrogen bonding (Figure 1b). Attractive monomers include “para”-bifunctionalized polyaromatic hydrocarbons, porphyrins and shape-persistent macrocycles.[15] Evidently, the main advantage of the present strategy over the supramolecular assembly approaches[13,14] is that the products can be isolated as discrete entities because of their covalent backbone. The most critical hurdle in this project is seen in the polymerizability of 1,8-disubstituted anthracenes, which have a hydrogen peri to the coupling sites and so far were never successfully used in SPC. We felt encouraged to seriously test this and the entire concept because of our recent multigram scale synthesis of highly pure 1,8-anthracene (**2**). which is obviously a “hairpin” monomer.[16]

p-Phenylene diboronates **1a** or **1b** were selected as simple counter monomers for these orienting studies (Scheme 1a). A related recently published approach by Morisaki and Chujo et al.[17] using a xanthane derivative rather than an anthracene led us disclose these findings in the present communication. It should be noted that on average they have obtained only low oligomeric products,[18] whereas one key interest of our work is to arrive at as high molar mass products as possible. Our results accidentally allowed an interesting and rather deep insight into the mechanism of SPC of this concrete case which will also be described.

Scheme 1. Alternating Copolymerization of Straight and Hairpin Monomers by SPC



The monomer syntheses were carried out according to literature procedures,[16,19,20] and the analytically pure compounds were obtained on a gram scale (see the Supporting Information). First, the straight **1a** and the hairpin **2** were subjected to SPC. Despite the two hexyloxy chains of **1a**, the product, oligomer/polymer **3a**, precipitated from the polymerization mixture as the reaction time progressed. The solubility of **3a** turned out to be so low that its molar mass could not be properly determined in common solvents. The chloroform-soluble part of the products could nevertheless be analyzed by MALDI-TOF mass spectrometry. Compared to the numerous unpublished such spectra of SPC products that were recorded over the years in the authors’ group, the present spectrum looks like a textbook example. Most remarkably, it shows all possible monomer combinations for the oligomers up to $n = 6$. There is no preferential formation of a dimer of **1a** and **2** to give an AB-type monomer, the prerequisite for considerations toward SPC operating according to a chain growth instead of a step-growth mechanism as was put forward by Yokozawa and others for some transition-metal-mediated cross-coupling polymerizations including certain SPC cases.[21] Furthermore, all oligomers

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[7] Zhang, A.; Sakamoto, J.; Schlüter, A. D. *Chimia* **2008**, *62*, 776.

[8] Sangvikar, Y. Sakamoto, J. Schlüter, A. D. *Chimia* **2008**, *62*, 678. See also ref 5 in which Figure 2 is used.

[9] For spontaneous chain folding, *e.g.*, in polyethylene, see: Keller, A.; O’Connor, A. *Nature* **1957**, *180*, 1289.

[10] For a review, see: Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893.

[11] See, for example: (a) Sastri, V. R.; Schulman, R.; Roberts, D. C. *Macromolecules* **1982**, *15*, 939. (b) Vogel, T.; Blatter, K.; Schlüter, A. D. *Makromol. Chem. Rapid Commun.* **1989**, *10*, 427. (c) Schürmann, B. L.; Enkelmann, V.; Löffler, M.; Schlüter, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 123. (d) Thomas, S. W.; Long, T. M.; Pate, B. D.; Kline, S. R.; Thomas, E. L.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 17976.

[12] See, for example: Yu, T.-B.; Bai, J. Z.; Guan, Z. *Angew. Chem., Int. Ed.* **2009**, *48*, 1097.

[13] See, for example: Dou, X.; Pisula, W.; Wu, J.; Bodwell, G. J.; Müllen, K. *Chem.—Eur. J.* **2008**, *14*, 240.

[14] See, for example: Ghadira, M. R. *Adv. Mater.* **1995**, *7*, 675.

[15] For a review, see: Grave, C.; Schlüter, A. D. *Eur. J. Org. Chem.* **2002**, 3075.

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[17] Morisaki, Y.; Imoto, H.; Miyake, J.; Chujo, Y. *Macromol. Rapid Commun.* **2009**, *30*, 1094.

[18] The highest molar masses given in ref 17 ($M_n = 4{,}000$; $P_n = 5.4$) refer to a fraction which represents 44% of the entire product mass. It is reasonable to assume that the remaining material is of lower molar mass and that the entire product has a representative P_n lower than 5.4. The authors additionally provide NMR-based molar mass data. For this purpose, the products were end-capped with appropriate groups. However, this method can overestimate the molar mass because it is not evident that all chains still have intact end groups at the time they were subjected to the end-capping reaction.

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[21] (a) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236. (b) Beryozkina, T.; Boyko, K.; Khanduyeva, N.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Simon, F.; Stamm, M.; Kiriy, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2695.

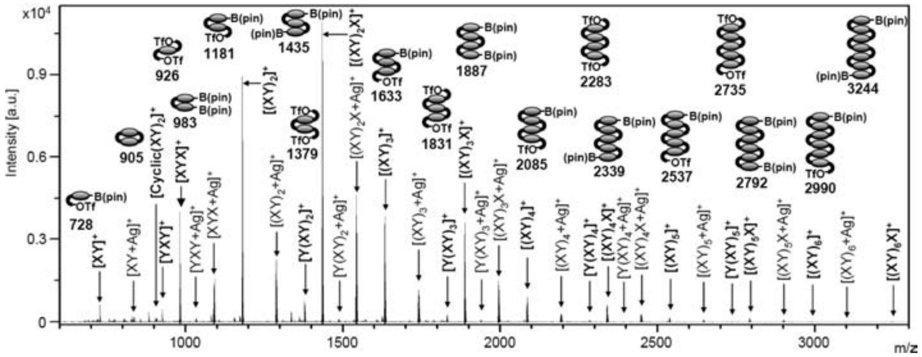

Figure 2. MALDI-TOF mass spectrum of the chloroform-soluble part of the SPC product **3a** (matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) with AgOTf) as fingerprint of step-growth mechanism (X = 2,5-dihexyloxy-1,4-phenylene, Y = 1,8-anthrylene, B(pin) = boron pinacolate, OTf = triflate).

have the two end groups, the commonly accepted mechanism of SPC requires (Figure 2). Thus, this spectrum supports the view that the growth mechanism of SPC is step-growth in this case. Also, the recently reported preferential 2-fold oxidative addition[22] does not seem to dominantly apply here. In contrast to the spectrum in Figure 2, related MALDI mass spectra often exhibit rather complex end group situations which do not normally allow any such mechanistic conclusions to be drawn. For a beautiful example by Janssen et al., see ref 23.

In order to let the products grow further without precipitation, monomer **1b** carrying the more flexible and longer tri(ethyleneoxy) chains was designed and used instead of **1a**. The polymerization was performed under previously reported SPC conditions (Pd[P(p-tolyl)$_3$]$_3$, NaHCO$_3$, THF/water, 80 °C) with or without additional use of a Buchwald ligand.[24,25] No precipitation was observed this time. The presence or absence of the additional ligand did not have a sizable effect. After workup, the crude product mixture was analyzed by gel permeation chromatography (GPC) using chloroform as eluent to give the trimodal main trace in Figure 3. Three fractions A−C were obtained by preparative GPC in isolated yields of 91% (508 mg) for A, 4% (21 mg) for B, and 5% (28 mg) for C.[26] ^{1}H NMR and MS analyses proved fraction C to consist of a ca. 1:1 atropisomeric mixture of the cyclic dimers **4** and **5** (Scheme 1b). The ^{1}H NMR signals of the tri(ethyleneoxy) chains of these products are shifted upfield in comparison to those of monomer **1b**, which is attributed to shielding effects caused by the adjacent anthrylene moieties. The side chains are obviously positioned over these units.

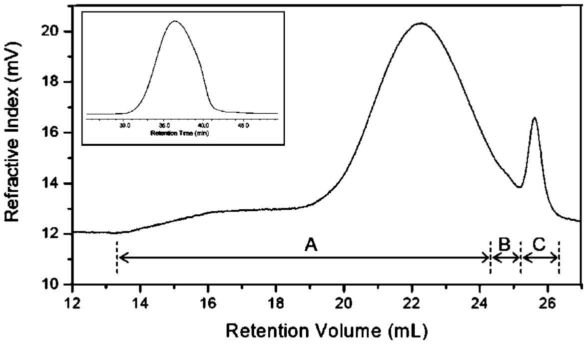

Figure 3. GPC elution curve of the crude product mixture **3b** from monomers **1b** and **2** using chloroform as eluent and an indication how the fractionation was performed. Inset: GPC chromatogram of fraction A using THF as eluent.

The cyclic dimers were used to assign the NMR spectrum of the higher molar mass fraction A (Figure 4). Though substantially broader, the signals of the polymer fraction appear at very similar chemical shifts, supporting the polymer structure **3b** as a whole but specifically also confirm its alternating character. In addition, the UV absorption spectrum of fraction A is nearly identical with the reference (Figure 5). The emission

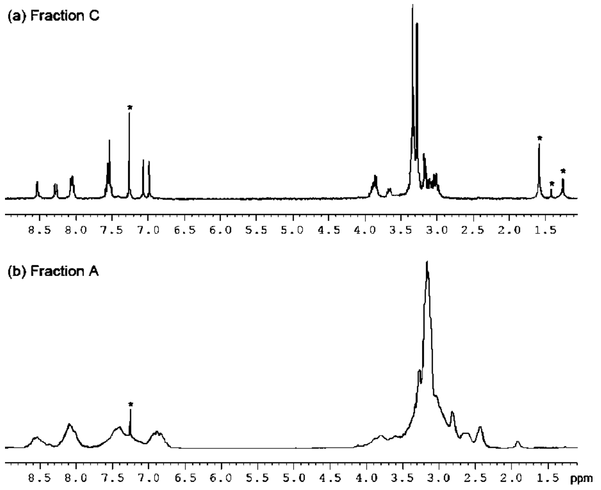

Figure 4. ^{1}H NMR spectra of fractions C (a) and A (b). Starred signals are from residual chloroform and impurities.

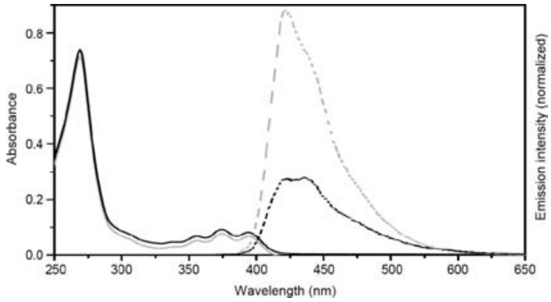

Figure 5. UV absorption (solid lines) and emission spectra (broken lines) of fractions A (black) and C (gray).

wavelength of fraction A is in a similar range as fraction C, but its overall intensity is lower than the reference's intensity at a similar concentration (Figure 5). This can be attributed to the lower rigidity of **3b** due to its open linear structure facilitating nonradiative deactivation. It should be mentioned that the high molar mass onset of fraction A's main peak was not separated off because it was expected to be caused by aggregates of individual chains which were not broken apart by chloroform. This was proven correct by rerecording this fraction now dissolved in THF. There were no detectable mass losses by filtering the THF solution through Millipore LCR filters (0.45 μm pore size) prior to injection into the GPC apparatus. As the inset in Figure 3 shows, a nearly monomodal elution curve was obtained. Based on polystyrene calibration, the average molar mass was estimated to $M_w = 14000$ ($P_w = 24$) and $M_n = 7000$ ($P_n = 12$). Note that this refers to 90% of the entire product mass and can therefore be considered almost representative. The same fraction was also analyzed by dynamic light-scattering (DLS) in hexafluoro-2-propanol (HFIP) and in THF. Whereas in HFIP a bimodal correlation function was observed with particle radii of $R_h = 3.3$ nm and $R_h = 65$ nm, in THF a monomodal decay led to a hydrodynamic radius of $R_h = 3.9$ nm. Obviously, the fast mode in HFIP solution corresponds to the radius measured in THF and represents the dimension of nonaggregated chains of polymer **3b**, whereas the slow mode is due to aggregate formation in HFIP. Assuming a rodlike conformation, a hydrodynamically effective diameter of **3b** of $d = 2.0$ nm, and a Schulz−Flory molar mass distribution function, a weight average contour length $L_w = 15-20$ nm is calculated.[27] Since the length per repeat unit is $l = 0.5$ nm, the weight average degree of polymerization P_w is in the range of $P_w \approx 30$ to 40 or $P_n \approx 15$ to 20, respectively. These numbers compare well to the GPC results. Obviously, the larger mass per unit length of **3b** as compared to the polystyrene standard (leading to a shorter contour length) is compensated by the larger hydrodynamic volume due to the increased chain stiffness of **3b**. Finally, fraction B was not investigated.

In conclusion, compound **2** with the *peri*-hydrogen atom between the two functional groups mediating the growth is in fact a viable monomer for SPC. For the counter monomer **1a** mostly insoluble material **3a** was obtained. The chloroform-soluble part, however, allowed an unexpectedly deep insight into the operative growth mechanism, proving it to be step-growth in nature. For monomer **1b**, soluble material **3b** was obtained which consisted of the new atropisomeric cyclic dimers **4** and **5** and polymeric material with a weight average molar mass of approximately 14000 g/mol referring to 90% of the entire product mass. The structure of the resulting polymer **3b** was confirmed by NMR, UV absorption, and emission spectroscopies. Given the complexity of the present system and the fact that no 1,8-disubstituted anthracenes or related compounds have ever been successfully subjected to SPC, polymer **3b** is considered a major step forward and suggests that truly high molar mass material may be achievable in the future after careful optimization. Whether the structural features realized in the present polymer are sufficient to enforce the aimed at secondary structure, which would be the one with all phenylene units forming a columnar stack, needs to be proven in the steps to come.

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Supporting Information Available: All experimental procedures including NMR and HR-MS for new compounds as well as the DLS correlation functions.This material is available free of charge via the Internet at http://pubs.acs.org.

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