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Facile Preparation of Poly(3-substituted thiophene) Block Copolymers by Nickel-catalyzed Deprotonative Polycondensation without External Generation of Thiophene Organometallic Species

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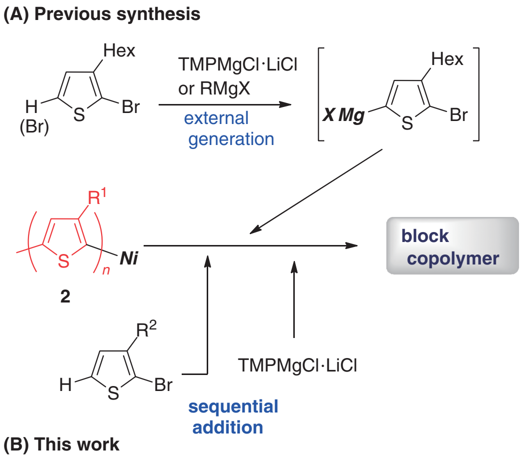
Thiophene-based block copolymers are synthesized by addition of bromothiophene and the Knochel–Hauser base (TMPMgCl•LiCl). Nickel-catalyzed deprotonative C–H coupling polycondensation of 3-substituted-thiophenes proceeds to give head-to-tail-type poly(3-substituted thiophen-2,5-diyl) bearing nickel at the polymer end. Block copolymers of thiophene derivatives are obtained by successive addition of 2-bromo-3-alkylthiophene and magnesium amide to a living polythiophene end. The use of nickel catalyst bearing an *o*-tolyl group gives the tolyl-group-terminated thiophene diblock copolymers in high efficiency. Triblock copolymer is also synthesized by the iterative addition of bromothiophene and TMPMgCl•LiCl.

Polythiophenes have recently attracted considerable attention in materials science. Regioregular thiophenes, which involve head-to-tail (HT) repeating units such as poly(3-hexylthiophene) (HT-P3HT), is of particular interest since the compound shows remarkable physical properties as materials such as organic TFT, thin-film organic solar cells, and conductive polymer materials.[1] In particular, π-conjugated block copolymers showing interesting properties such as self-organization, microphase separation, and so on are of much interest.[2] Thus, development of a practical synthetic method for π-conjugated block copolymers is an important issue in polymer syntheses.[3]

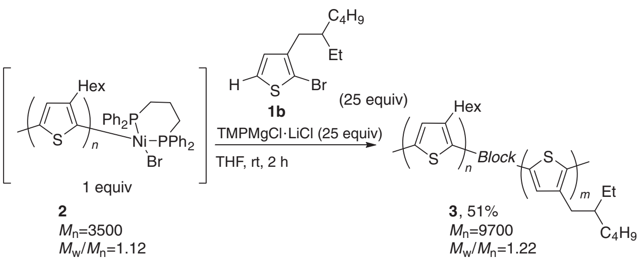
In general, block copolymers of polythiophene have been synthesized by the Kumada–Tamao–Corriu or Negishi cross-coupling polymerization.[3] Yokozawa and McCullough independently reported that such cross-coupling proceeds via a chain-growth polymerization mechanism to afford π-conjugated polymers with low polydispersity and controlled molecular weight, which is well recognized as GRIM polymerization.[4,5] Since the reaction proceeds in a catalyst-transfer manner, which enables undergoing chain-growth polymerization despite polycondensation,[6] block copolymerization can be performed by the addition of a thiophene organometallic species into the polymerization mixture.[5b,7] Thus, generation of the metalated thiophene must be performed under external inert conditions as shown in Scheme 1 (path A) because of the highly moisture-sensitive characteristics of organometallic thiophenes. Accordingly, various block-copolymers have been synthesized by the addition of the thus externally formed organometallic monomers. Although the use of a more stable main group monomer such as boron and tin, which have been employed to give block copolymers of poly(fluorene)s and poly(*p*-phenylene)s by the palladium-catalyzed Suzuki–Miyaura cross-coupling polymerization,[8] is an alternative choice, inferior step efficiency that requires extra preparation steps would be the trade-off toward the air and moisture-sensitivity.



Scheme 1.

On the other hand, during our studies on the deprotonative polycondensation of thiophene by transition-metal catalysis, we learned that employment of 2-halo-3-substituted thiophene instead of 2,5-dihalothiophene and the use of the Knochel–Hauser base, TMPMgCl•LiCl[9] (chloromagnesium 2,2,6,6-tetramethylpiperidide lithium chloride salt) have been the key for successful polythiophene synthesis.[10,11] We have found also that magnesium amide does not interfere with propagation of the polymer.[10c] This finding markedly contrasts with the observation that a Grignard reagent employed for the metalation in debrominative GRIM polymerization serves as a terminating agent at the living polymer end. We considered that block copolymerization of thiophenes can be achieved by the separate addition of a premonomer 2-halo-3-alkylthiophene and deprotonating base to the living polymer solution as Scheme 1 (path B). The method, if successful, can realize remarkably facile block copolymer synthesis and thereby no more external preparation and transfer of sensitive organometallic species are required. We herein describe that facile synthesis of polythiophene block copolymers is achieved by successive addition of thiophene premonomer and the Knochel–Hauser base (TMPMgCl•LiCl) independently.

When 2-bromo-3-(2-ethylhexyl)thiophene (**1b**) and the Knochel–Hauser base TMPMgCl•LiCl was successively added to the reaction mixture of P3HT (**2**), which was prepared by the polymerization of 2-bromo-3-hexylthiophene (**1a**): $M_n = 3500$ ($M_w/M_n = 1.12$) in a deprotonative manner[10a] and whose polymer end was believed to possess a C–Ni bond, extension



Scheme 2.

Table 1. Synthesis of diblock copolymers using [NiCl(*o*-tol)(dppp)] as a catalyst[a]

1st polymerization		2nd polymerization		Yield[c] /%
–R^1	M_n[b] (M_w/M_n)	–R^2	M_n[b] (M_w/M_n)	
n-Hex (**1a**)	4900 (1.25)	2-ethylhexyl (**1b**)	9700 (1.39)	57 (***o*-tol-3**)
n-Hex (**1a**)	4900 (1.25)	*n*-dodecyl (**1c**)	7300 (1.55)	75 (***o*-tol-4**)
2-ethylhexyl (**1b**)	3300 (1.14)	*n*-Hex (**1a**)	10500 (1.38)	60 (***o*-tol-5**)
n-dodecyl (**1c**)	6100 (1.24)	*n*-Hex (**1a**)	8200 (1.47)	50 (***o*-tol-6**)

[a] The first polymerization was carried out with [NiCl(*o*-tol)(dppp)] (0.01 mmol), 2-bromo-3-substituted thiophene (0.25 mmol), and TMPMgCl•LiCl (0.25 mmol) in 5 mL of THF at 0 °C, and the second polymerization was carried out with 2-bromo-3-substituted thiophene (0.25 mmol), and TMPMgCl•LiCl (0.25 mmol). [b] M_n and M_w/M_n values were estimated by SEC analysis using $CHCl_3$ as an eluent using standard polystyrenes. [c] Isolated yield. [d] The first polymerization was carried out with [NiCl(*o*-tol)(dppp)] (0.01 mmol), 2-bromo-3-hexylthiophene (0.3 mmol), and TMPMgCl•LiCl (0.3 mmol) in 5 mL of THF at 0 °C and the second polymerization was carried out with 2-bromothiophene (0.1 mmol), and TMPMgCl•LiCl (0.1 mmol).

of the molecular weight was observed by SEC analysis ($M_n = 9700$ ($M_w/M_n = 1.22$)) without serious broadening of the molecular weight distribution suggesting the formation of the corresponding block copolymer poly(3-hexylthiophene-2,5-diyl)-*block*-poly[3-(2-ethylhexyl)thiophene-2,5-diyl] (**3**) in 51% isolated yield as shown in Scheme 2.

We next synthesized diblock copolymers using [NiCl(*o*-tol)(dppp)] as a catalyst,[12] with which *o*-tolyl group was introduced into the polymer end. The first polymerization was carried out with [NiCl(*o*-tol)(dppp)], which was in situ generated by [NiCl(*o*-tol)(PPh_3)$_2$] and DPPP, 25 equiv of 2-bromo-3-hexylthiophene (**1a**), and 25 equiv of TMPMgCl•LiCl at 0 °C for 10 min to afford poly(3-hexylthiophene) ***o*-tol-2** with M_n of 4900 ($M_w/M_n = 1.25$). Following addition of 25 equiv of 2-bromo-3-(2-ethylhexyl)thiophene (**1b**) and 25 equiv of TMPMgCl•LiCl, to the polymerization reaction mixture induced the second polymerization at 0 °C for 2 h to give tolyl-terminated poly(3-hexylthiophene)-*block*-poly[3-(2-ethylhexyl)-thiophene] (***o*-tol-3**) in 57% yield with M_n of 9700 ($M_w/M_n = 1.39$). Under similar polymerization conditions to give ***o*-tol-3**, the use of several other 3-substituted-2-bromothiophenes allowed conversion into diblock copolymers as shown in Table 1. Use of a thiophene derivative bearing *n*-dodecyl group **1c** also afforded the block copolymer ***o*-tol-4** in 75% yield. Inverse block copolymerization toward **3** similarly afforded poly{[3-(2-ethylhexyl)thiophene]-*block*-(3-hexylthiophene)} (***o*-tol-5**) in good yield.

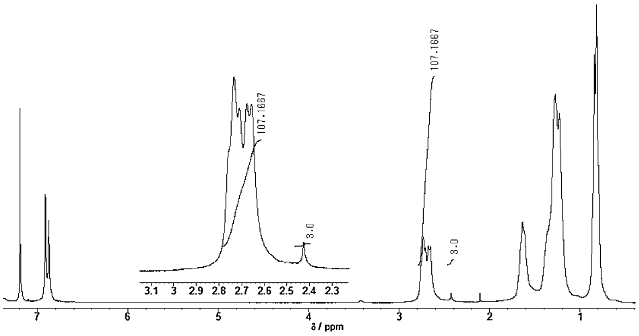
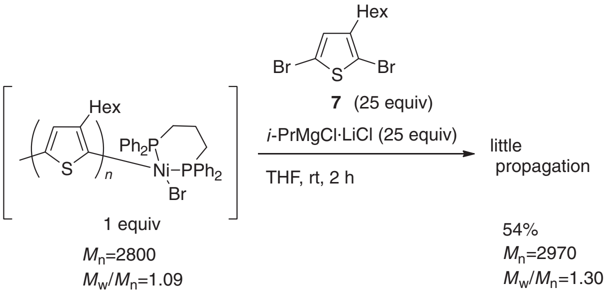


Figure 1. ^{1}H NMR spectrum of tolyl-terminated poly(3-hexylthiophene)-*block*-poly[3-(2-ethylhexyl)thiophene] **3**.

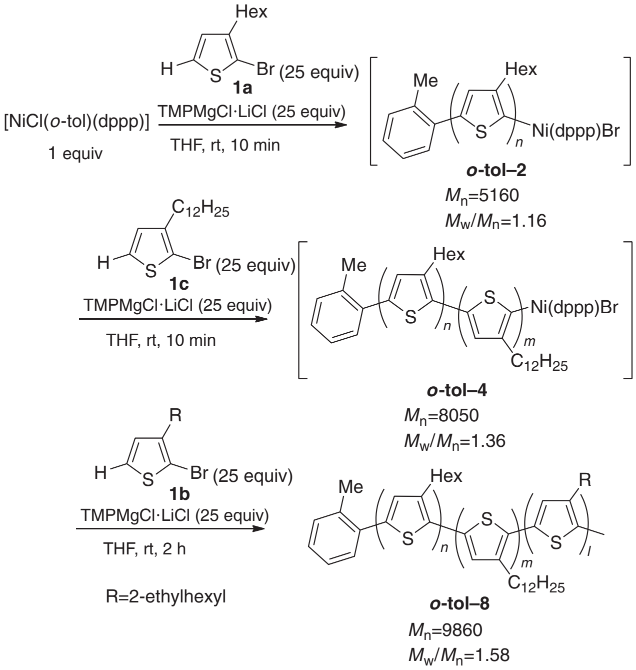


Scheme 3.

Figure 1 shows the ^{1}H NMR spectrum of the tolyl-terminated block copolymer ***o*-tol-3**, in which the methyl group derived from the terminal tolyl group was clearly observed at ca. 2.4 ppm. The average degree of polymerization was estimated to be 53 by the calculation of the integration ratio of the methyl (tolyl) and the methylene (thiophene side chain) protons. The M_n value was found to be relatively close compared with the result by SEC analysis ($M_n = 9700$).

In contrast with the above-mentioned successful block copolymerization, attempted in situ GRIM polymerization by the further addition of **7** and then *i*-PrMgCl•LiCl was found to be unsuccessful resulting in little incorporation of the second monomer after stirring at room temperature for 2 h probably because undesired preferential termination at the prepolymer end might take place by the addition of the Grignard reagent (Scheme 3).

Triblock copolymer was also synthesized by the similar protocol. Successive addition of 3-hexylthiophene **1a** (25 equiv) and TMPMgCl•LiCl (25 equiv) to a THF solution of [NiCl(*o*-tol)(dppp)] induced the first polymerization to result in giving ***o*-tol-2** with $M_n = 5160$ ($M_w/M_n = 1.16$). Then, 25 equiv of dodecylthiophene **1c** and 25 equiv of TMPMgCl•LiCl were similarly added to the reaction mixture to obtain the diblock copolymer ***o*-tol-4** with $M_n = 8050$ ($M_w/M_n = 1.36$). Further polymerization of **4** with 2-bromo-3-(2-ethylhexyl)thiophene



Scheme 4.

(**1b**) and the Knochel–Hauser base afforded the triblock copolymer ***o*-tol-8** in 51% yield with $M_n = 9860$ ($M_w/M_n = 1.58$) (Scheme 4).

In conclusion, we have shown that thiophene-based diblock and triblock copolymers were synthesized by the sequential addition of premonomer 2-bromo-3-substituted thiophene and the Knochel–Hauser base. Since no external preparation of thiophene organometallic species sensitive to moisture and oxygen is necessary for copolymerization, the synthetic procedure is quite simple and practical allowing synthesis of block copolymers in a considerably facile manner. The use of [NiCl(*o*-tol)(dppp)] as a catalyst as well as initiating agent gives highly regioregular polythiophene block copolymers with well-defined end groups with desired molecular weight and polydispersity in a controllable manner. With the present synthesis, several additional copolymers involving different aromatic structures could also be obtained.[13]

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