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Highly Stable Semiconducting Polymers Based on Thiazolothiazole

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Introduction

Semiconducting polymers are important class of materials in organic electronics and have been attracting much attention in both academic and industrial research today. Great advantages in these plastic materials as compared to inorganic or organic small molecular materials are that they are highly solution-processable (printable) and give high quality thin films, which could lead to manufacturing large-area and flexible electronic devices.[1–4] Use of semiconducting polymers in organic field-effect transistors (OFETs) is of particular interest, because OFET is a fundamental component in organic electronic applications and can drive a number of important electronic applications.[5–8] In OFETs, semiconducting polymers are required to have good processability, high charge carrier mobility, such as >0.1 cm^2/(V s), and high stability, such as high on/off ratios of >1 × 10^5.[9–16] More importantly, long-term air stability (environmental stability) is a crucial factor for the practical use of the devices that would not require passivation or encapsulation process.

Recently, we have reported on the synthesis, structural studies and OFET application of new semiconducting polymers consist of thiophene and thiazolothiazole, poly(2,5-bis(3-alkyl-5-(3-alkylthiophen-2-yl)thiophen-2-yl)-thiazolo[5,4-*d*]thiazole)s (PTzQTs, Scheme 1).[17,18] The polymers, having strong π-stacking due to the donor–acceptor structure along the backbone, exhibit high mobilities of up to 0.30 cm^2/(V s) and high on/off ratios of 1 × 10^7. These polymers with long alkyl side chains (dodecyl and tetradecyl) also showed good environmental stability. However, in contrast to the polymers with long side chain that showed some degradation in the OFET performance, one with shorter hexyl side chain showed significantly more degradation: mobilities and current on/off ratios of the polymers with dodecyl and tetradecyl side chains decreased for ~20% and for 1 to 2 orders of magnitude, whereas those of the hexyl polymer decreased for 50% and for 4 orders of magnitude, respectively. Nevertheless, the hexyl polymer is still more stable than familiar regioregular poly(3-hexylthiophene). We speculate that the rationale for the high stability in the longer side chain polymers in this system is that the polymer chains are highly ordered and the side chains are densely packed, which may protect the backbones away from ambient air (oxygen and/or humidity). Thus, although these polymers give relatively deep HOMO levels, essentially the backbone should not be an optimal structure to afford sufficient stability. In this paper, we describe the design, synthesis, and characterization of new thiazolothiazole-thiophene copolymer systems that exhibit improved environmental stability along with high mobility in OFETs.

An improvement of environmental stability can be achieved by lowering the HOMO level of the materials. Incorporation of an electron deficient ring in the backbone

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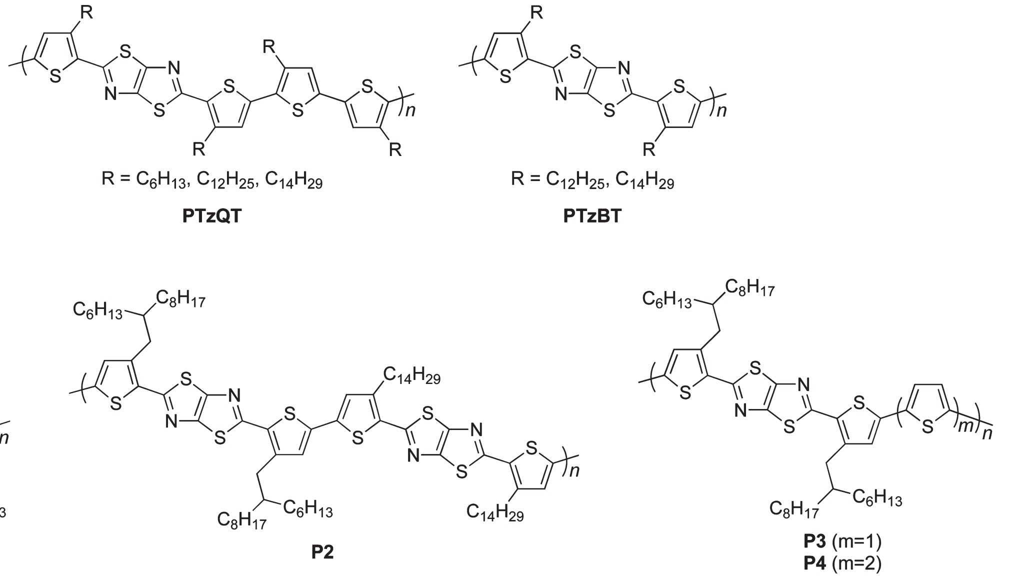
Scheme 1. Structures of Thiazolothiazole-Thiophene Copolymers Synthesized in the Previous Reports (PTzQT and PTzBT), and in This Report (P1−P4)



is an effective methodology to lower the HOMO levels of the polymers, as proven by several systems including PTzQTs.[17,19−22] HOMO levels can also be lowered by decreasing the density of the electron-rich group in the unit structure.[9,15,16,20] Poly(2,5-bis(3-dodecylthiophen-2-yl)-thiazolo[5,4-d]thiazole) PTzBT (Scheme 1), incorporating fewer alkylthiophenes that are electron-donating moieties than PTzQT, is therefore expected to afford a deeper HOMO level relative to PTzQT. However, PTzBT with linear alkyl side chain is an insoluble polymer and thereby is not solution-processable.[17] In order to solubilize this polymer, PTzBT with branched alkyl chain (2-hexyldecyl) was originally synthesized (P1) in this work. However, P1-based OFET showed very low mobility (in the order of 1×10^{-4} cm^2/(V s)), which is likely due to the absence of π-stacking, evident from the X-ray studies, perhaps caused by a steric repulsion of the bulky branched alkyl side chains. In order to reduce this steric effect, we then carefully designed and synthesized new thiazolothiazole-thiophene copolymers with keeping the deep HOMO level; "alternating copolymer" of PTzBT with hexyldecyl side chain block and tetradecyl side chain block (P2), and copolymers of nonsubstituted thiophene or bithiophene and the P1 structure (P3 and P4).

Results and Discussion

Synthetic routes to the polymers are depicted in Scheme 2. Comonomer 1 was polymerized with comonomer 2, 3, and 4 via the Stille coupling reaction to give corresponding copolymers P1−P4 as dark metallic solids. These polymers are well soluble in chloroform and chloro- or 1,2-dichlorobenzene at room temperature, and P1 is even soluble in hexane. Chemical, optical, and electrochemical properties of the polymers are summarized in Table 1. Molecular weight of the polymers (M_n) is 7.6−13.7 kg/mol. Thermal analyses by differential scanning calorimetry (DSC) showed no phase transition peaks in all polymers. Thin film absorption maxima (λ_{max}) correspond to 0−0 and 0−1 transitions were observed at 600−630 nm and at 560−580 nm (Figure 1), respectively. P1 and P2 showed similar λ_{max} to PTzQT-14, whereas λ_{max} of P3 and P4 blue-shifted possibly due to the rotational freedom of the unsubstituted thiophene rings, which prevents the delocalization of π-electron systems. As a result, the bandgaps of P3 and P4 (1.9 eV), evaluated from the onset of absorption spectra, appeared to be larger than those of P1 and P2 (1.8 eV). Cyclic voltammetry were employed to evaluate the HOMO level of the polymers. All polymers showed reversible oxidation (p-doping) processes in the voltammograms (Figure 2). As expected, HOMO levels of P1−P4 (5.2−5.3 eV), calculated by using

Scheme 2. Synthetic Routes to New Thiaozolothiazole-Thiophene Copolymers P1−P4

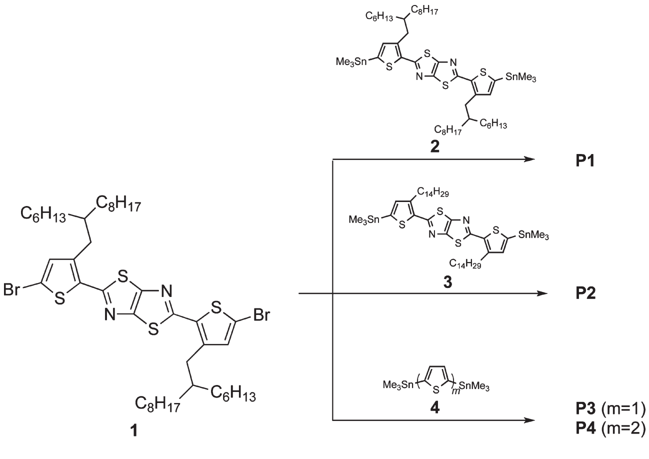


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Table 1. Polymer Properties

					d spacing (Å)[e]	
polymer	M_n (kg/mol)/ PDI[a]	λ_{max} (nm)[b]	E_g (eV)[c]	HOMO (eV)[d]	lamella	$\pi-\pi$ stacking
P1	13.7/1.8	575, 624	1.8	5.3	18.2	3.5
P2	10.0/1.6	575, 627	1.8	5.2	21.0	3.6
P3	7.7/1.4	567, 605	1.9	5.2	18.4	3.6
P4	7.6/1.5	563, 610	1.9	5.2	16.7	3.5
PTzQT-14	18.9/2.1	582, 629	1.8	5.1	21.1	3.5

[a] Number averaged molecular weights (M_n) and polydispersity index (PDI) determined by a high-temperature GPC using the polystyrene standard. [b] Absorption maxima for polymer thin films. [c] Band gaps determined from the onsets of absorption peaks of thin films. [d] HOMO levels evaluated from the onsets of oxidation potentials of thin film using cyclic voltammetry. The potentials are determined by using Fc/Fc$^+$ as standard based on the assumption that the redox couple of Fc/Fc$^+$ is 4.4 eV relative to vacuum (Fc = ferrocene). [e] d spacings correspond to the lamellar structures (100) and $\pi-\pi$ stackings (010).

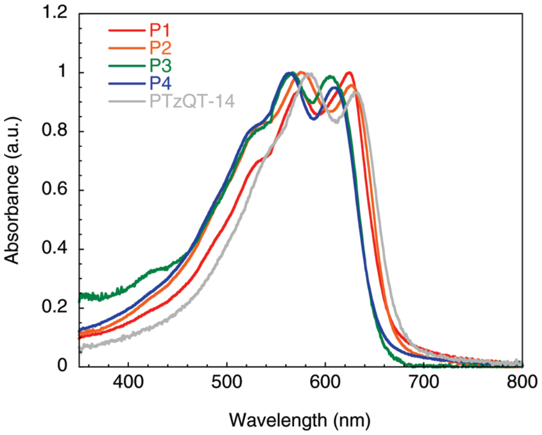

Figure 1. UV−vis absorption spectra of polymer thin films.

onset oxidation, were found to be 0.1−0.2 eV larger than that of PTzQT-14 (5.1 eV), which should be a necessary consequence of lesser electron donating nature of P1−P4 relative to PTzQT-14. These relatively deep HOMO levels are expected to lead to improved oxidative stability in this system.

The microstructures of the polymers were investigated by grazing incidence wide-angle X-ray scattering (GIWAXS) using their thin films prepared on octyltrichlorosilane (OTS) treated SiO_2/Si substrates followed by thermal annealing at 150 °C. Figure 3 depicts the two-dimensional GIWAXS patterns (a)−(d), out-of-plane (e) and in-plane (f) profiles. P1−P4 show four orders for (h00) scatterings in the out-of-plane direction indicating the formation of highly ordered lamellar sheets. However, as seen in the 2D patterns, all these scattering arcs diffuse widely, even appear in the in-plane direction, and additionally (200), (300), and (400) peaks appear to be relatively weak, both of which imply that the lamellar sheets are more disordered as compared to PTzQT-14.[18,23] The lamellar d spacing of P1 was evaluated to be 18.2 Å (q = 0.34 Å^{-1}), which seems to be determined by the decyl part of the branched hexyldecyl side chain. In the meantime, the d spacing of P2 was 21.0 Å (q = 0.38 Å^{-1}), similar value to PTzQT-14, which seems to be determined by the tetradecyl side chain. Increasing the number of thiophene rings in the repeating unit, P3 to P4, decreased the d spacing, 18.4 to 16.7 Å, perhaps as a result of the promoted intercalation of the branched alkyl chains into the widened space between the substituted thiophene rings in adjacent backbones. For $\pi-\pi$ stacking structures that can be seen from the in-plane scattering (Figure 3f), the arcs diffuse widely as is the case in the out-of-plane, which also indicates that the polymer lamella are disordered (tilted with diffuse angles from the surface normal). From the in-plane profile of P1, although the $\pi-\pi$ stacking distance is very close (3.5 Å), the peak intensity relative to that of the (100) peak appear to be very low as compared to P2−P4, indicating the absence of $\pi-\pi$ stacking. P2−P4, on the other hand, show visible peak intensities for $\pi-\pi$ stacking with distances of 3.5−3.6 Å, indicating the existence of $\pi-\pi$ stacking order, most probably due to the reduced steric repulsion. These GIWAXS results are in good agreement with the OFET performance of the polymers as will be discussed below.

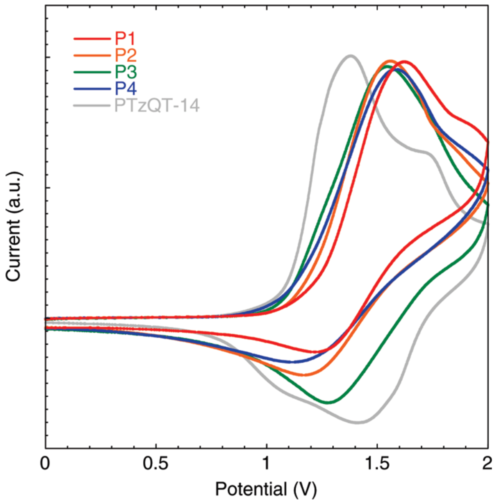

Figure 2. Cyclic voltammograms of polymer thin films.

OFET properties of the polymers were evaluated using bottom gate bottom contact devices fabricated by drop casting the room temperature chloroform solution of the polymers on the SiO_2 gate dielectric treated by octyltrichlorosilane (OTS). The devices were subsequently annealed for 30 min at 150 °C in a glovebox under nitrogen. It is interesting that even though P2−P4 do not exhibit phase transition peaks in thermal analysis, they showed an increase in the on-current after annealing, leading to the increased mobility and on/off ratio. This increase is rationalized by the X-ray diffraction (XRD) measurements that the diffraction patterns gave more intense and narrower lamellar peaks after annealing (see Figure S2 in the Supporting Information). For P1, however, annealing did not improve the device performance, which is consistent with the fact that XRD patterns did not change by annealing. Figure 4 provides the typical current−voltage characteristics of annealed P2 devices with L = 25 μm, where I_{DS}, V_{DS}, and V_G represent source−drain current, source−drain voltage, and gate voltage, respectively. Table 2 summarizes the transistor characteristics of all the polymers after annealing. Threshold voltages (V_t)

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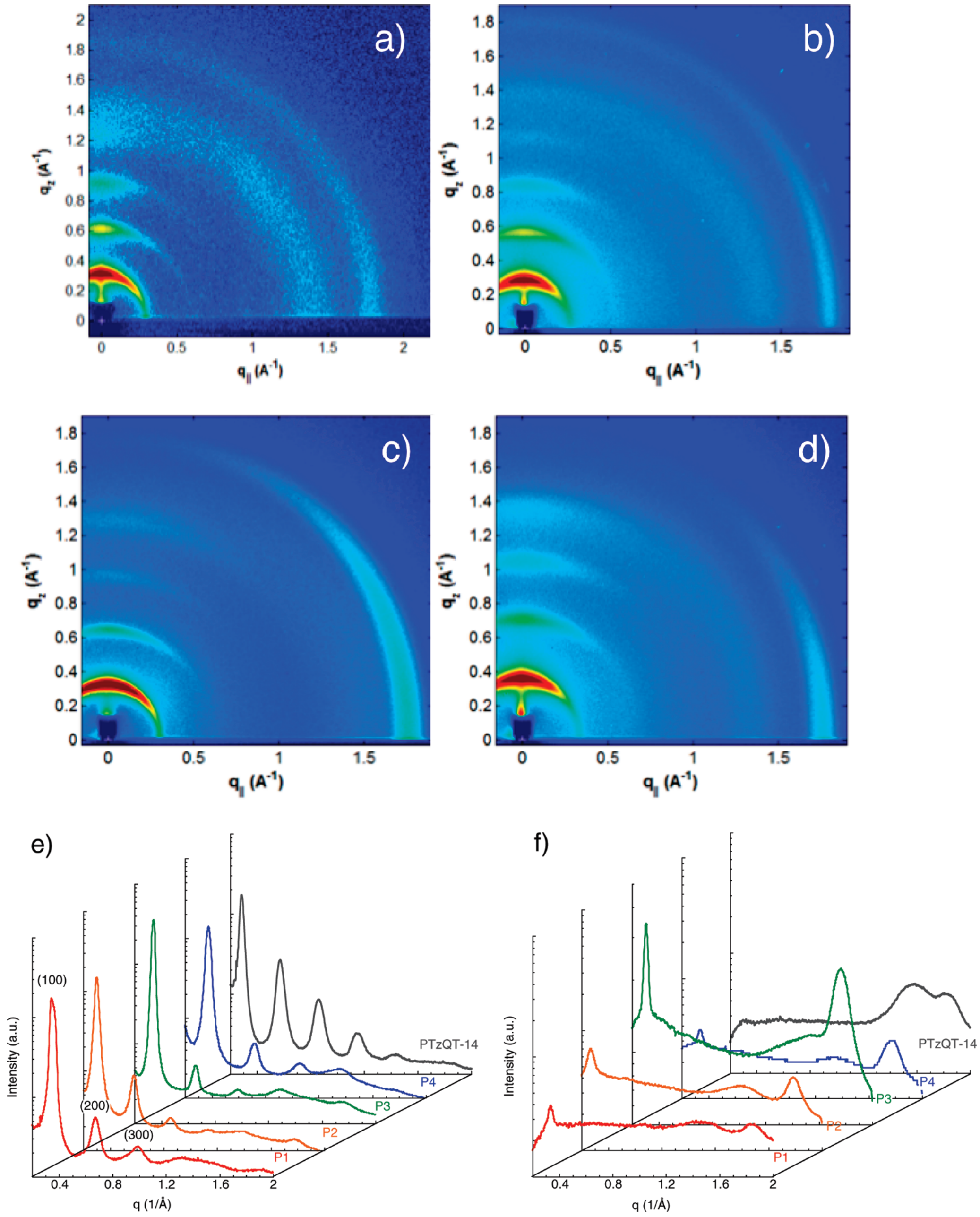

Figure 3. GIWAXS patterns of drop-cast polymer thin films annealed at 150 °C: 2D patterns of (a) P1, (b) P2, (c) P3, and (d) P4 and profiles of (e) out-of-plane and (f) in-plane directions.

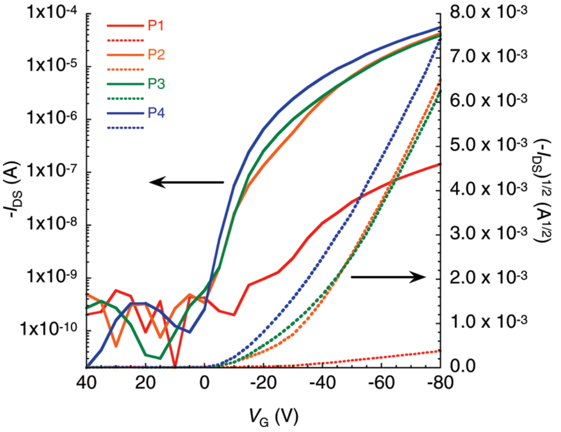

Figure 4. Transfer curves of the polymer devices.

of polymer devices were −20 to −40 V. P1 showed very low mobilities on the order of 1×10^{-4}, which can be understood by the fact that the $\pi-\pi$ stacking is absent. In contrast, P2−P4 showed relatively high mobilities of reaching 0.1 $cm^2/(V\ s)$ with average mobilities of 0.6−0.7 $cm^2/(V\ s)$, which are close to those of PTzQT-14 measured under the same conditions (Table 2), apparently originate from the enhanced $\pi-\pi$ stacking as compared to P1. These mobilities in P2−P4 are surprisingly high, considering that these polymers are disordered against the device surface normal (not uniformly edge-on oriented). As we have reported, designing "transistor paint" by using donor−acceptor type semiconducting polymers with very strong $\pi-\pi$ stacking can provide high mobilities in disordered or "amorphous" structures (without high crystalline structure), when sufficient

Table 2. Transistor Properties of the Polymers

polymer	μ_{max} ($cm^2\,V^{-1}\,s^{-1}$)[a]	μ_{ave} ($cm^2\,V^{-1}\,s^{-1}$)[b]	I_{on}/I_{off}
P1	2.7×10^{-4}	1.4×10^{-4} ($\pm 0.88 \times 10^{-4}$)	1×10^3 to 1×10^4
P2	0.13	0.070 (± 0.038)	1×10^5 to 1×10^6
P3	0.12	0.076 (± 0.031)	1×10^5 to 1×10^7
P4	0.10	0.063 (± 0.018)	1×10^5 to 1×10^6
PTzQT-14	0.13	0.10 (± 0.019)	1×10^5 to 1×10^6

[a] Maximum mobilities from more than 10 different devices. [b] Average mobilities and standard deviations in parentheses from more than 10 different devices.

Table 3. Changes in Mobilities and on/off Ratios of the Polymer Devices after 50 Days in Ambient Conditions

	μ ($cm^2/(V\,s)$)		I_{on}/I_{off}	
polymer	initial	50 days[a]	initial	50 days[a]
P1	0.0002	0.0002	2×10^3	3×10^3
P2	0.047	0.041	7×10^5	7×10^5
P3	0.049	0.051	2×10^7	1×10^6
P4	0.079	0.070	4×10^5	7×10^5
PTzQT-14	0.13	0.067	5×10^5	9×10^4

[a] Polymer devices were stored for 50 days at rt, in air, with 30−50% humidity.

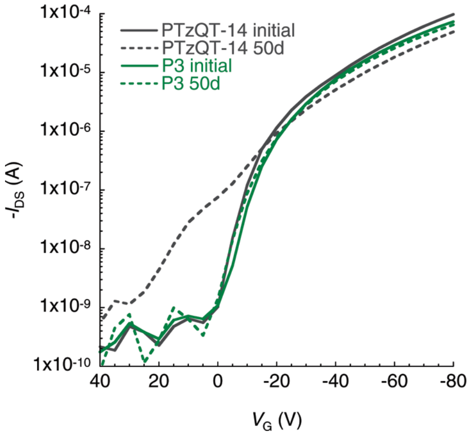

Figure 5. Changes in transfer characteristics of P3 (green lines) and PTzQT-14 (gray lines) devices: solid and dotted lines correspond to the characteristics for initial and after 50 days of storage, respectively.

$\pi-\pi$ stacking distance is preserved macroscopically throughout the thin films.[17−19,24] Current on/off ratios are also listed in Table 2. Although P1 showed relatively low on/off ratios, 1×10^3 to 1×10^4, due to the low on-current, P2−P4 showed high on/off ratios of up to 1×10^6 or 1×10^7.

Furthermore, we investigated the long-term air stability of polymer devices, in which devices were stored in air, in the dark, at 30−50% humidity, for 50 days. Figure 5 represents the changes in transfer characteristic of P3 and PTzQT-14 devices. In PTzQT device, on- and off-current slightly decreased and increased, respectively, resulting in some detriment in the mobility. In contrast, the P3 device showed no noticeable increase in off-current and V_t shift, and thus no change in the mobility, indicative of excellent environmental stability (showed negligible changes in the mobility). All other polymers synthesized here also showed excellent environmental stability, as summarized in Table 3. Since high OFET performance can usually be kept under low humidity,[11,20,25] these high performance after the long-term storage, most likely due to the deepened HOMO levels, should be remarkable.

Experimental Section

Materials. Monomers **1**, **2**, and **3** were synthesized according to the previous paper.[17] 2,5-bis(trimethylstannyl)thiophene[26] and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene[27] (monomer **4**) were synthesized according to the reported procedure. ^{1}H NMR spectra were measured in $CDCl_3$ as the deuterated solvent using BRUKER Avance 300 NMR spectrometer.

Synthesis of P1. A solution of **1** (274 mg, 0.3 mmol), **2** (324 mg, 0.3 mmol), tris(dibenzylideneacetone)dipalladium (0) (5.5 mg, 0.006 mmol), tri-*o*-tolylphosphine (7.3 mg, 0.024 mmol) in 10 mL of anhydrous chlorobenzene was refluxed for 3 days under a N_2 atmosphere. After being cooled to 50 °C, the reaction solution was poured into 200 mL of methanol containing 5 mL of hydrochloric acid and stirred for 5 h. The precipitated dark brown solid was then subjected to sequential Soxhlet extraction with methanol and hexane to yield 362 mg of dark brown metallic product after removing hexane and drying in vacuo (yield = 80%). ^{1}H NMR ($CDCl_3$, δ ppm): 7.04 (br, 2H), 2.70 (br, 4H), 2.14 (br, 2H), 1.30 (br, 48H), 0.90 (br, 12H).

Synthesis of P2. A solution of **1** (133 mg, 0.15 mmol), **3** (150 mg, 0.15 mmol), tris(dibenzylideneacetone)dipalladium (0) (2.7 mg, 0.003 mmol), tri*o*-tolylphosphine (3.6 mg, 0.012 mmol) in 8 mL of anhydrous chlorobenzene was refluxed for 3 days under a N_2 atmosphere. After being cooled to 50 °C, the reaction solution was poured into 200 mL of methanol containing 5 mL of hydrochloric acid and stirred for 5 h. The precipitated dark brown solid was then subjected to sequential Soxhlet extraction with methanol and hexane to remove the low-molecular-weight fraction of the material. The residue was extracted with chloroform to yield 174 mg of dark brown metallic product after removing chloroform and drying in vacuo (yield = 80%). ^{1}H NMR ($CDCl_3$, δ ppm): 7.04 (br, 4H), 2.90 (br, 8H), 2.14 (br, 2H), 1.86 (br, 4H), 1.30 (br, 92H), 0.90 (br, 18H).

Synthesis of P3. This polymer was synthesized as described for **P2** using 0.2 mmol of comonomers, respectively, to yield 153 mg of dark brown metallic product (yield = 92%). ^{1}H NMR ($CDCl_3$, δ ppm): 7.30 (br, 2H), 7.04 (br, 2H), 2.70 (br, 4H), 2.10 (br, 2H), 1.30 (br, 48H), 0.90 (br, 12H).

Synthesis of P4. This polymer was synthesized as described for **P1** using 0.2 mmol of comonomers respectively to yield 160 mg of dark brown metallic product (yield = 86%). ^{1}H NMR ($CDCl_3$, δ ppm): 7.92 (br, 2H), 7.34 (br, 2H), 7.00 (br, 2H), 2.71 (br, 4H), 2.13 (br, 2H), 1.30 (br, 48H), 0.91 (br, 12H).

Conclusion

We designed and synthesized new thiazolothiazole-thiophene copolymers to improve environmental stability. The polymers demonstrated excellent stability as they maintained the initial OFET performance after 50 days in air in relatively high humidity, most probably

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due to the successfully deepened HOMO levels. In addition, although the polymer chains are disordered and thus have amorphous nature that perhaps originates from branched alkyl side chains, they showed high mobilities of reaching 0.1 cm^2/(V s). The polymers described here are another examples of a system that exhibit high mobility without high crystalline and long-range ordered structures. Given with these unique features, along with excellent solubility, the polymers are quite promising materials in printable electronics with high processability, high mobility, and excellent stability.

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Supporting Information Available: Experimental procedures, AFM images, and transistor characteristics of the polymer thin films (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.