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Effects of the ethoxy and diethylamino substituent on the electrochemical and conducting properties of poly[(silanylene)oligothienylenes]

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Abstract

Polymers composed of alternating ethoxypropyl- or diethylaminohexylsilanylene and oligo(2,5-thienylene) units, $[(SiRX)(C_4H_2S)_m]_n$ (**3a**–**5a**, R = Pr, X = OEt, $m = 3$–5; **5b**, R = Hex, X = Et$_2$N, $m = 5$) were synthesized and their properties were investigated in comparison with those of the diethylsilanylene analogs, $[(SiEt_2)(C_4H_2S)_m]_n$ (**3c**–**5c**, $m = 3$–5). The UV and emission bands, and anodic peaks in cyclic voltammograms of polymers **3a**–**5a** and **5b** are at almost the same energies as those of the respective **3c**–**5c** with the same number of m. However, polymers **3a**–**5a** and **5b** were found to be much more stable toward electrochemical oxidation and reduction, as compared with **3c**–**5c** with the same number of m. Polymers **3a**–**5a** became conducting upon doping with FeCl$_3$ with the conductivities in the order of 10^{-2}–10^{-1} S cm^{-1}, similar to the diethylsilanylene analogs **3c**–**5c**. In contrast, polymer **5b** exhibited highly conducting properties when doped with I$_2$, whose conductivity was determined to be 4.4 S cm^{-1}. Photoconducting properties of polymer **4a** and **4c** are also described. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Organosilicon polymer; Oligothiophene; Electrochemistry; Conducting polymer

1. Introduction

There has been interest in the chemistry of polymers composed of an alternating arrangement of an organosilicon and π-electron unit in the backbone [1], because they may be used as functionality materials, such as organic semiconductors [2], hole-transporting materials [3], photoresists [4], and heat-resistant materials [5]. Of those, polymers having oligothienylene as the π-electron unit have been investigated extensively concerning their conducting properties in the doped states [2,6–8]. In addition, silanylene oligothienylene polymers have received current attention regarding their applications to electrodevices. Hadziioannou and

coworkers have demonstrated that a silanylene-hexa(2,5-thienylene) alternating polymer can be used as the emitter of the long lived electroluminescent (EL) devices [9]. Similar use of the organosilanylene–oligothienylene polymers for light emitting devices have been studied recently by Sheradsky et al. [10] and Yoshino et al. [11]. It has been also reported that a disilanylene–quarterthienylene alternating polymer shows visible-light photoconduction and the photocurrent is enhanced by doping the polymer with C$_{60}$ [12].

Recently, we have synthesized polymers with alternating mono-, di-, or trisilanylene and oligo(2,5-thienylene) units, $[(SiR_2)_x(C_4H_2S)_m]_n$ (R = Me, Et, $x = 1$–3, $m = 2$–5, **3c**–**5c**, **3d**–**5d**, **5e**, see below), and investigated their optical, conducting, and hole-transporting properties, in order to learn how the polymer structure affects the electronic states and functionalities of the polymers [7,8]. Interestingly, the polymer elec-

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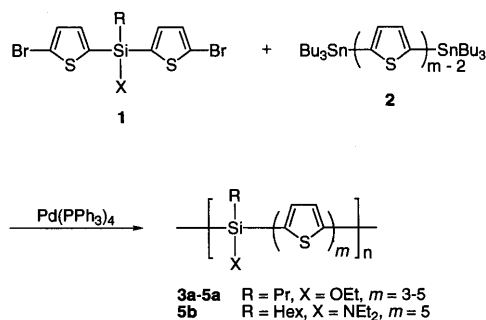
Scheme 1.

tronic states depend strongly on the oligothienylene chain length (m), and the band gap energies of the polymers decrease along m. The organosilanylene chain length, however, has little effect on the electronic states of the polymer in solution phase.

To evaluate how the nature of the substituent at the silicon atom of this type of polymer influences the polymer properties, we synthesized silanylene-oligo(2,5-thienylene) alternating polymers with an ethoxy- or diethylamino-substituents on the silicon atom (**3a–5a** and **5b**), and studied their optical, electrochemical, and conducting properties, in comparison with those of diethylsilanylene and tetraethyldisilanylene analogs (**3c–5c** and **3d–5d**). In a series of these polymers, the arabic figures correspond to the number of thienylene units (m).
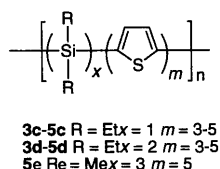

2. Results and discussion

Ethoxy- and diethylaminosilanylene polymers (**3a–5a** and **5b**) were synthesized by Stille type coupling reactions [13,14] of bis(bromothienyl)silanes (**1**) with bis(tributylstannyl)mono-, bi-, and terthiophene (**2**) in 45–60% yield (Scheme 1 and Table 1). The polymers are dark brown solids and soluble in aromatic solvents, chlorocarbons, and ethers, but insoluble in hydrocarbons. The molecular weights of the polymers, determined by GPC, relative to polystyrene standards, are $M_{\mathrm{w}} = 10\,000$ to $27\,000$ as shown in Table 1. Ethoxysilanylene polymers **3a–5a** are air stable and can be handled without any special care, while diethylaminosilanylene polymer **5b** is highly moisture sensitive, and standing it in air for several hours resulted in the formation of insoluble solids, probably due to cross linking reactions, forming interchain siloxane bridges.

As can be seen in Table 1, the UV and emission bands, and anodic peaks in cyclic voltammograms (CV) of polymers **3a–5a** and **5b** are at almost the same energies as those of **3c–5c** with the same number of thienylene groups in a repeating unit (m), indicating that the electronic states of the polymers are little affected by the nature of the substituent. However, polymers **3a–5a** and **5b** were found to be much more stable toward electrochemical oxidation, as compared with simple alkyl derivatives.

It has been reported previously that when thin films of di- and trisilanylene polymers (**3d–5d** and **5e** above) were prepared on an ITO electrode by spin coating and the electrodes were subjected to potential-sweep experiments in an acetonitrile–Et$_4$NBF$_4$ solution, the oxidation occurred in two stages and the CV revealed more or less the same features: i.e. the first wave is reversible and the second irreversible [15]. The oxidation peak
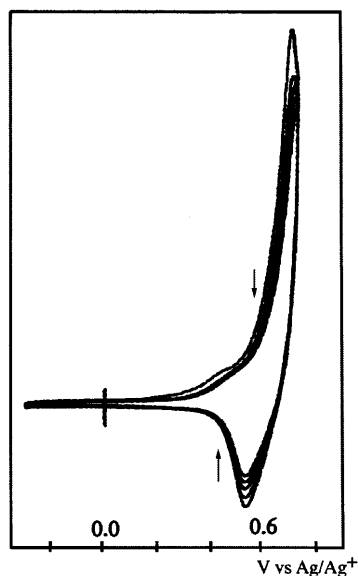
Table 1
Synthesis and properties of silanylene–oligothienylene polymers, $[(\mathrm{SiRX})(\mathrm{C_4H_2S})_m]_n$

Polymer	m	R	X	Yield (%) [a]	M_{w} ($M_{\mathrm{w}}/M_{\mathrm{n}}$) [b]	Absorption [c] $\lambda_{\max}$ (nm) ($\varepsilon \times 10^{-3}$)	Emission [d] λ_{em} (nm)	Conductivity [e] S (cm^{-1})
3a	3	Pr	OEt	56	14 000 (2.0)	382 (26)	425	4.5×10^{-2}
4a	4	Pr	OEt	45	24 000 (2.5)	411 (25)	468	2.3×10^{-2}
5a	5	Pr	OEt	60	10 000 (1.7)	434 (37)	563	1.1×10^{-1}
5b	5	Hex	NEt$_2$	59	27 000 (1.8)	435 (51)	497	3.6×10^{-4}
								4.4 [f]
3c [g]	3	Et	Et		17 000 (2.2)	384 (17)	423	5.5×10^{-2}
4c [g]	4	Et	Et		11 000 (1.7)	414 (35)	469	2.1×10^{-2}
5c [g]	5	Et	Et		5000 (2.0)	425 (63)	498	2.3×10^{-1}

[a] After reprecipitation from chloroform–hexane.

[b] Determined by GPC, relative to polystyrene standards.

[c] In THF.

[d] In dioxane.

[e] Polymer film doped with FeCl$_3$.

[f] Doped with I$_2$.

[g] Reference [10].

Fig. 1. CV profile of a spin coated film of polymer **5a** in a range of -0.4–0.7 V vs. Ag | Ag$^+$.

Fig. 2. CV profile of a cast film of polymer **5a** in a range of -2.4–1.2 V vs. Ag | Ag$^+$.

is not so stable as expected and the peak current gradually decreases after repetitive scanning in the same range [15c].

We also examined the voltammetric behavior of monosilanylene derivatives **3c**–**5c** and found that the films of these polymers exhibit approximately the same behaviors as those for di- and trisilanylene derivatives with the corresponding *m*.

To our surprise, however, introduction of an ethoxy- or diethylamino substituent onto the silicon atom drastically improved the stability of the electrochemically oxidized polymer films. Thus, the CV of the cast film of **5a** on ITO exhibits a quite stable redox at 0.64/0.46 V versus Ag/Ag$^+$ in the acetonitrile–Et$_4$NBF$_4$ solution, as shown in Fig. 1 [16]. The electrochemical stability, estimated by decrease of the peak current, increases in the order of **3c**–**5c** < **3a** < **4a** = **5b** < **5a**. Interestingly, the film of **5a** also shows a redox couple in the cathodic region as shown in Fig. 2. Although the reasons for these phenomena are unclear yet, we assume at least that electron donating ethoxy or amino group can stabilize the Si–thienylene bonds in the positively doped polymers.

Like other silanylene–oligothienylene polymers [6–8], the present polymers became conducting upon doping with FeCl$_3$ and I$_2$. As shown in Table 1, the conductivities of the doped films of ethoxysilanylene polymers **3a**–**5a** are at the same level of diethylsilanylene polymers **3c**–**5c** and tend to increase along *m*, as observed for **3c**–**5c**. Although the conductivity of FeCl$_3$ doped **5b** was determined to be much lower than those for **3a**–**5a** and **3c**–**5c**, it exhibited surprisingly higher conductivity of 4.4 S cm^{-1} on doping with I$_2$. This is presumably due to the complex formation between the amino group and iodine. Similar enhancement of the conductivities of I$_2$ doped polycarbosilanes [17] and polysilanes [18] by introduction of an amino group has been reported previously.

We also studied photoconducting properties of the polymer films of **4a** and **4c**. The photocurrent was defined as observed photocurrent minus observed dark current, on the device with the structure of ITO–polymer–Au. Like optical and electrochemical properties, the photoconducting properties of **4a** and **4c** were quite similar and no clear changes of the photoconducting properties due to the difference of the substituent on the silicon atom were observed. Furthermore, they are comparable with those of poly[(tetraethyldisilanylene)tetra-2,5-thienylene] (**4d**) [12]. As illustrated in Fig. 3, the maximum photoconductivity of polymers **4a** and **4c** appear at about 470 nm, close to the absorption edges of the polymers and at longer wavelength by ca. 60 nm from the absorption maximum. This is probably due to the fact that almost all incident light would be absorbed in the vicinity of the illuminated surface of the film in the region of the strong absorption band of

potential shifts towards positive direction and the redox becomes more stable, as *m* increases. As a typical example, when the film of disilanylene polymer **5d** with the thickness of 0.2 μm was polarized anodically, the films were wholly dissolved into the solution after few scans beyond the second wave (0–1.2 V vs. Ag | Ag$^+$), whereas a considerably stable redox was observed for the thicker film ($\geqq 1$ μm) by potential sweeping in the first wave region (0–0.75 V). We have clarified that the film surface dissolves partially at the first scanning due to cleavage of Si–C or Si–Si bonds, but a new protecting layer is then formed on the surface to prevent the further degradation of polymer [15c]. However, the film

the polymers. Similar phenomena have been reported already for polymer **4d** [12].

3. Conclusions

We have synthesized silanylene–oligothienylene alternating polymers **3a**–**5a** and **5b** with an ethoxy or diethylamino group at the silicon atom, respectively, by the Stille type reactions. The investigations of the polymers with respect to their UV absorption and emission spectra and CV indicates that the ethoxy or diethylamino substituent does not considerably affects the polymer electronic states but stabilizes the polymer films toward electrochemical oxidation and reduction. Introduction of an amino substituent in **5b** led to significant enhancement of polymer conductivity when doped with I_2. On the basis of these results, it is reasonably demonstrated that the ethoxy and diethylamino substitution on the silicon atom seems to provide an opportunity to modify the polymer functionalities.

In addition, the ethoxy group may be replaced with the other organic group by nucleophilic substitution, as we have reported previously for poly[(ethoxysilanylene)phenylenes] [19]. The methodology involving preparation of ethoxy substituted silanylene oligothienylene polymers followed by replacement of the ethoxy group seems to be applicable to the synthesis of variously substituted silanylene oligothienylene polymers.

4. Experimental

4.1. General

All reactions were carried out under a dry nitrogen atmosphere. THF and ether used as the solvents were dried over a sodium–potassium alloy and distilled just

Fig. 3. Wavelength dependence of photocurrent density of polymer **4a** with the absorption spectrum of the thin film.

before use. Hexane and toluene used for reprecipitation of polymer **5b** were distilled from $LiAlH_4$ and stored over molecular sieves before use. ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were recorded on JEOL model JNM-EX 270 and JNM-EX 400 spectrometers. UV spectra were measured on a Hitachi U-3210 spectrophotometer. IR-spectra were measured on a Perkin–Elmer 1600-FT infrared spectrometer. Molecular weights of polymers were determined by GPC, using THF as the eluent, and are relative to polystyrene standards. The usual work up used for the following synthetic experiments involves hydrolysis of the mixture, separation of the organic layer, drying the organic phase over anhydrous magnesium sulfate, and evaporation of the solvent.

4.2. Synthesis of monomers

4.2.1. Bis(bromothienyl)ethoxypropylsilane (**1**, R = Pr, X = OEt)

To a mixture of 5-bromothienyl-2-magnesium bromide, prepared from 20.0 g (82.6 mmol) of 2,5-dibromothiophene and an equimolar amount of magnesium in 50 ml of THF, was added 10.1 g (40.9 mmol) of propyltriethoxysilane at room temperature (r.t.) and the resulting mixture was heated to reflux for 2 days. After the usual work up, the organic products were distilled under reduced pressure to give 5.58 g (31% yield) of the title compound: b.p. 110–115°C/1 mmHg. ^{1}H-NMR: δ 0.98 (t, $J = 7.2$ Hz, 3H), 1.04–1.10 (m, 2H), 1.19 (t, $J = 6.9$ Hz, 3H), 1.12–1.56 (m, 2H), 3.77 (q, $J = 6.9$ Hz, 2H), 7.13 (br s, 4H). ^{13}C-NMR: δ 16.4, 17.9, 18.1, 18.2, 59.8, 119.0, 131.4, 136.7, 137.2. ^{29}Si-NMR: δ −14.7. MS m/z 438 (M$^+$ for ^{79}Br). Anal. Calc. for $C_{13}H_{16}Br_2OS_2Si$: C, 35.46; H, 3.66. Found: C, 35.41; H, 3.80%. In this reaction, (bromothienyl)propyldiethoxysilane and tris(bromothienyl)propylsilane were also found to be formed in about 20 and 10% yields, respectively, which were removed readily by distillation.

4.2.2. Bis(bromothienyl)(diethylamino)hexylsilane (**1**, R = Hex, X = NEt₂)

To a mixture of 5-bromothienyl-2-lithium, prepared from 14.0 g (57.8 mmol) of 2,5-dibromothiophene and 37.0 ml (56.9 mmol) of a 1.54 M *n*-butyllithium–hexane solution in 80 ml of ether, was added 7.30 g (28.5 mmol) of dichloro(diethylamino)hexylsilane at −80°C. The mixture was allowed to warm to r.t. and stirred over night. After the resulting inorganic salts were filtered and the solvent was evaporated, the residue was distilled under reduced pressure to give 7.00 g (48% yield) of the title compound: b.p. 160–165°C/1 mmHg. ^{1}H-NMR: δ 0.83–1.35 (m, 19H), 2.89 (q, $J = 6.9$ Hz, 4H), 7.05 (d, $J = 3.6$ Hz, 2H), 7.09 (d, $J = 3.6$ Hz, 2H). ^{13}C-NMR: δ 14.1, 15.1, 15.6, 22.6, 23.2, 31.3, 33.2, 39.7, 118.1, 131.2, 136.8, 139.3. ^{29}Si-NMR: δ −18.4.
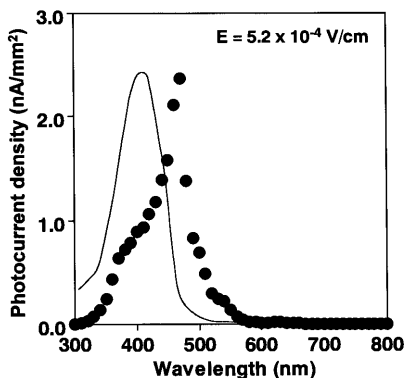
MS *m/z* 507 (M$^+$ for ^{79}Br). Anal. Calc. for C$_{18}$H$_{27}$Br$_2$NS$_2$Si: C, 42.44; H, 5.34; N, 2.75. Found: C, 42.80; H, 4.85; N, 2.52%. This monomer is moisture sensitive and must be stored in a dry atmosphere. Standing it in air resulted in the formation of insoluble materials.

4.3. Synthesis of polymers

4.3.1. Polymers 3a–5a

To a mixture of 2,5-dilithiothiophene, prepared from 0.774 g (3.20 mmol) of 2,5-dibromothiophene and 4.20 ml (6.40 mmol) of a 1.54 M *n*-butyllithium–hexane solution in 10 ml of ether, was added 2.47 g (7.60 mmol) of tributyltin chloride in 15 ml of THF at −10°C. After heating the mixture to reflux overnight, 1.41 g (3.20 mmol) of bis(bromothienyl)propylethoxysilane (**1**, R = Pr, X = OEt) and 0.100 g (2.70 mol%) of Pd(PPh$_3$)$_4$ were added to the mixture and the mixture was further refluxed for 2 days. After the usual work up, the resulting organic products were reprecipitated from chloroform/hexane to give 0.650 g (56% yield) of polymer **3a**: m.p. 58–65°C. IR 1074 cm^{-1} (νSi–O). ^{1}H-NMR: δ 0.84–1.26 (m, 10H), 3.84 (q, *J* = 6.9 Hz, 2H), 7.08–7.32 (m, 6H). ^{13}C-NMR: δ 16.6, 18.0, 18.3, 18.5, 59.7, 125.0, 133.6, 136.2, 137.6, 143.7. ^{29}Si-NMR: δ − 13.4. Anal. Calc for C$_{17}$H$_{18}$OS$_3$Si: C, 56.31; H, 5.00. Found: C, 54.46; H, 4.98%. Lower carbon content determined by combustion analysis than the theoretical value is often observed for organosilicon polymers (see Ref. [18] and references there in). This would be due to the formation of carbon-containing ceramics, such as β-SiC during the analysis. Polymers **4a** and **5a** were obtained as described above, using dilithiobithiophene or dilithioterthiophene instead of dilithiothiophene, respectively. Data for **4a**: m.p. 77–85°C. IR 1074 cm^{-1} (νSi–O). ^{1}H-NMR: δ 0.88–1.28 (m, 10H), 3.84 (q, *J* = 6.9 Hz, 2H), 7.07–7.31 (m, 8H). ^{13}C-NMR: δ 16.6, 18.0, 18.3, 18.5, 59.8, 124.4, 125.0 (2C), 133.6, 136.0, 136.3, 137.6, 143.7. ^{29}Si-NMR: δ − 13.4. Anal. Calc. for C$_{21}$H$_{20}$OS$_4$Si: C, 56.71; H, 4.53. Found: C, 55.70; H, 4.50%. Data for **5a**: m.p. 68–80°C. IR 1073 cm^{-1} (νSi–O). ^{1}H-NMR: δ 0.87–1.26 (m, 10H), 3.85 (q, *J* = 6.9 Hz, 2H), 7.07–7.33 (m, 10H). ^{13}C-NMR: δ 16.6, 18.0, 18.3, 18.5, 59.8, 124.4 (3C), 125.0 (2C), 133.6, 136.0, 136.3, 137.6, 143.7. ^{29}Si-NMR: δ − 13.5. Anal. Calc. for C$_{25}$H$_{22}$OS$_5$Si: C, 56.99; H, 4.27. Found: C, 56.53; H, 4.27%.

4.3.2. Polymer 5b

To a mixture of 5,5″-dilithiothiophene, prepared from 0.812 g (2.00 mmol) of 5,5″-dibromoterthiophene and 2.60 ml (4.00 mmol) of a 1.54 M *n*-butyllithium–hexane solution in 20 ml of THF, was added 1.40 g (4.30 mmol) of tributyltin chloride at − 10°C. After heating the mixture to reflux overnight, 1.02 g (2.00 mmol) of bis(bromothienyl)(diethylamino)hexylsilane (**1**, R = Hex, X = NEt$_2$) and 0.100 g (4.30 mol%) of Pd(PPh$_3$)$_4$ were added to the mixture and the mixture was further refluxed for 1 day. The resulting inorganic salts were filtered and the solvent was evaporated. Reprecipitation of the residue from toluene/hexane in an atmosphere of dry argon gave 0.703 g (59% yield) of polymer **5b**: m.p. > 300°C. ^{1}H-NMR: δ 0.87–1.46 (m, 19H), 2.98 (q, *J* = 6.9 Hz, 4H), 7.07–7.16 (m, 10H). ^{13}C-NMR: δ 14.1, 15.2, 15.9, 22.6, 23.4, 31.4, 33.2, 39.8, 124.3, 124.7, 125.0, 136.0, 136.3, 137.3, 143.0. ^{29}Si-NMR: δ − 17.6. Anal. Calc. for C$_{30}$H$_{33}$NS$_5$Si: C, 60.46; H, 5.58; N, 2.35. Found: C, 59.36; H, 5.36; N, 2.01%. Polymer **5b** is highly moisture sensitive and must be stored in an atmosphere of dry argon.

4.4. CV measurements

CV measurements for the disilanylene–oligothienylene polymers were carried out using a three electrodes system in an acetonitrile solution containing 100 mM of tetraethylammonium tetrafluoroborate as the supporting electrolyte. Thin solid films of the polymers were prepared by spin coating or casting of the polymer solution in chloroform on ITO working electrodes. An Ag/0.1 M AgClO$_4$ electrode and a Pt plate were used as the reference and counter electrode, respectively. Peak potential was determined in a sweep rate of 50 mV s^{-1}. The current–voltage curve was recorded on a Hokuto Denko HAB-151 potentiostat/galvanostat.

4.5. Measurement of conductivities of polymer films doped with FeCl$_3$ or I$_2$

A benzene solution of a polymer was cast to a thin film on a glass plate. After the solvent was evaporated, the film was dried in vacuo overnight and then held over FeCl$_3$ or I$_2$ powder which was placed in a glass vessel. Doping with FeCl$_3$ vapor was performed by heating the bottom of the glass vessel at 150°C under reduced pressure (1 mmHg) for 24–48 h, while that with I$_2$ vapor was carried out at r.t. under atmospheric pressure. The conductivities of the polymers were determined by the four-probe method as listed in Table 1.

4.6. Measurements of photoconductivities

A polymer film (ca. 4 μm) was prepared by spin coating of the toluene solution on an ITO coated quartz plate. A counter Au electrode (ca. 0.2 μm) was deposited on the polymer surface by vacuum evaporation under 1×10^{-3} Pa at a deposition rate of 1 nm s^{-1}. The cell was placed in an optical cryostat (Technolo Kogyo Co. Ltd., CN-3) evacuated to 10^{-1} Pa. Steady state photocurrent measurements were carried

out using an electrometer with an applied voltage between the Au and ITO electrodes. Monochromic light from 300 W Xe lamp through a monochromator was used as a light source for irradiation. The light intensity was monitored by a silicon photodiode (Hamamatsu Photonics, S1337-66BQ).

Acknowledgements

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[16] The redox of **5a** was found to be much more stable in acetonitrile containing Et_4NClO_4 as the supporting electrolyte, and the value of the peak current remained in more than 70% level of the maximum value even after 400 cycles of sweeping between 0–0.75 V.

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