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# Oxidized states of soluble oligothiophenes and polythiophenes

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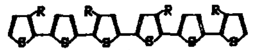
Sexi-, novi-, duodeci- and quindecithiophenes with hexyl groups were prepared by a reductive coupling reaction of dibromodihexylterthiophene with an activated nickel(0) reagent and purified by liquid chromatography. The structures were determined by $^1$H n.m.r. spectra, g.p.c. data, and elemental analyses. The comparison of their $\pi$–$\pi^*$ transitions with those of poly(alkylthiophene)s showed that the polymers had a similar effective conjugation length to the novithiophene derivative. The oligothiophenes were oxidized with stoichiometric amounts of $FeCl_3$ in methylene chloride and characterized by u.v.-vis.-n.i.r. absorption and e.s.r. spectroscopy. The first oxidation of the oligothiophenes yielded cation radicals (polarons), which were spread over thiophene rings between 6 and 8. The absorption spectra of the first-oxidized oligothiophenes were similar to those of the poly(alkylthiophene)s oxidized in solution. The further oxidation of the oligothiophenes produced a heavily oxidized species, such as dications (bipolarons), trication radicals, or poly(cation radical)s. The absorption spectra of the heavily oxidized oligothiophenes were quite different from those of the oxidized poly(alkylthiophene)s. These results indicated that oxidized species in poly(alkylthiophene) solutions were also cation radicals. Furthermore, the absorption spectra of the oxidized quindecithiophene derivative suggested the presence of the cation radical in the second-electron oxidized state. Copyright © 1996 Elsevier Science Ltd.

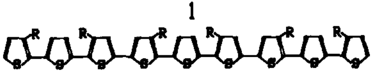
**(Keywords: oligothiophenes; poly(alkylthiophene); preparation)**

## INTRODUCTION

$\pi$-Conjugated polymers have attracted much attention in view of both fundamental interest and potential application, because they demonstrate the insulator–metal transition upon doping (oxidizing or reducing) and are promising candidates for batteries[1], display devices[2], and molecular electronic devices[3]. The conduction mechanism containing carrier generation upon doping has been studied intensively. Most of the polymers were infusible and insoluble in organic solvents owing to the stiffness of the main chains consisting of conjugated bonds. These properties prevent the satisfactory elucidation of the mechanism. Although poly[3-(long alkyl)-thiophene]s having good solubility and considerable conductivity in oxidized states were prepared[4,5], n.m.r. measurements of the poly(alkylthiophene)s showed that the polymers contained about 25 mol% head-to-head configuration, indicating that the effective conjugation length is limited by twists of the polymer chain[6–8]. Recently, several researchers prepared oligothiophenes that have well-defined structures, and studied the oxidized or neutral oligomers as model compounds of conducting polythiophenes[9–14]. The oligothiophenes underwent two-step oxidation to produce cation radicals (polarons) or $\pi$-dimers of those in the first step and dications (bipolarons) in the second step. However, we found that the first and the second oxidation of more soluble hexyl-substituted sexithiophene (**1**) yielded cation radicals and trication radicals, respectively[15]. In addition, we have reported on the preparation of **1**, hexyl-substituted novithiophene (**2**), duodecithiophene (**3**), and quindecithiophene (**4**) using a convenient procedure and the properties of the one-electron oxidized oligothiophenes in rapid communication[16,17]. This paper describes the properties of not only the one-electron oxidized but also the heavily oxidized oligothiophenes and a comparison of their properties with those of oxidized poly[3-(long alkyl)thiophene]s in detail.



**1**



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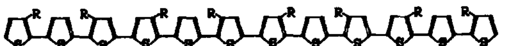

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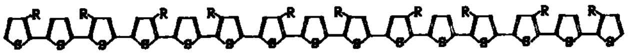

**4**

R=$C_6H_{13}$

## EXPERIMENTAL

### *Material*

5,5″-Dibromo-3,3″dihexyl-2,2′:5′,2″-terthiophene (**5**) was synthesized by bromination of the corresponding

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dihexylterthiophene[18] with *N*-bromosuccinimide in a 1 : 1 mixture of chloroform and acetic acid at ambient temperature in 94.8% yield. $^1$H n.m.r. (270 MHz, $CDCl_3$) (chemical shift (ppm) from tetramethylsilane): 0.88 (t; 6H), 1.25–1.35 (m; 12H), 1.65 (m; 4H), 2.70 (t; 4H), 6.90 (s; 2H), 6.99 (s; 2H).

The hexyl-substituted oligothiophenes **1**, **2**, **3** and **4** were prepared by a reductive coupling reaction of the dibromide **5** according to a similar procedure described for the preparation of $\alpha$-octithiophenes[19]. The dibromide **5** (3.00 g, 5.22 mmol) in 20 ml of hexane was added dropwise to an activated nickel(0) reagent prepared from anhydrous $NiCl_2$ (109 mg, 0.84 mmol), Zn (2.53 g, 38.7 mg-atoms), triphenylphosphine (850 mg, 3.2 mmol), and 2,2′-bipyridine (126 mg, 0.85 mmol) in 75 cm$^3$ of *N*,*N*-dimethylformamide. The mixture was heated at 70°C for 5 h. The resulting mixture was poured into 500 cm$^3$ of 15% HCl methanol solution and then the obtained precipitate was filtered off. Liquid chromatography of the residue (hexane-benzene/silica gel) afforded **1** (40 mg, 1.8%), **2** (60 mg, 2.8%), **3** (30 mg, 1.4%) and **4** (40 mg, 1.8%). In practice oligothiophenes with higher molecular weights were separated by liquid chromatography, but were not identified accurately.

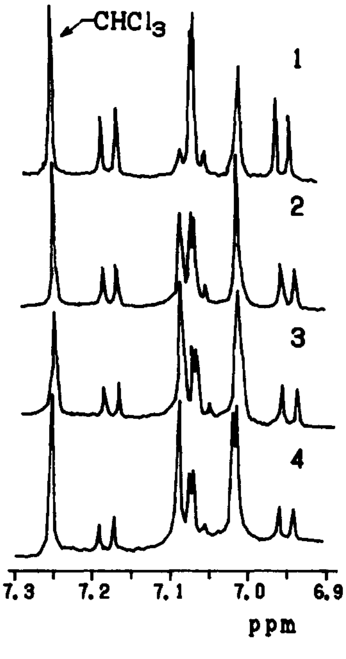

**Figure 1** $^1$H n.m.r. spectra for aromatic protons of hexyl-substituted oligothiophenes **1**–**4**

### *Measurements*

$^1$H n.m.r. experiments were performed on a JEOL GSX270 spectrometer in the pulse Fourier transform mode. G.p.c. data were measured using a Shimazu FCV-1008 instrument equipped with a Shodex K-803 column.

The solutions of the oligothiophenes (9.1–3.6 × $10^{-5}$ M) and ferric chloride (2.2 × $10^{-3}$ M) were prepared in freshly distilled dry dichloromethane or chloroform and the ferric chloride solution was added stepwise to the oligomer solutions. For u.v.-vis.-n.i.r. and e.s.r. measurements, a fraction of the mixture solutions in variously oxidized states was transferred to a quartz cell and a capillary tube, respectively, and then was meticulously sealed by the use of a paraffin film. These procedures were carried out under nitrogen at ambient temperature and the spectra of the mixture solutions recorded immediately. U.v.-vis.-n.i.r. absorption spectra were obtained with a JASCO Ubest-570 spectrometer. E.s.r. spectra were detected using a JEOL JES-FE 3X X-band spectrometer at low microwave power to avoid microwave saturation effects. The e.s.r. spin concentration of the solutions was calibrated by a standard dichloromethane solution of 1,1-diphenyl-2-picrylhydrazyl.

## RESULTS AND DISCUSSION

### *Preparation*

The four hexyl-substituted oligothiophenes **1**, **2**, **3** and **4** were prepared by a reductive coupling reaction of the dibromoterthiophene **5** and purified with a liquid chromatograph. The isolated hexyl-substituted oligothiophenes were identified by $^1$H n.m.r. spectroscopy, g.p.c. and elemental analysis. *Figure 1* shows the 270 MHz $^1$H n.m.r. spectra for aromatic protons of the hexyl-substituted oligothiophenes at 27°C. The peaks at $\delta = 7.26$ are due to $CHCl_3$ as an impurity in chloroform-d. All spectra show two moderate doublet peaks at $\delta = 6.94$ and 7.18. The coupling constant ($J = 5.0$ Hz) was consistent with $^1$H n.m.r. data of 3,3′-dimethyl-2,2′-bithiophene[20]. Therefore, these doublet peaks are assigned to the 4- and 5-positions on the terminal 2-substituted 3-alkylthiophene. The peaks in the region of $\delta = 7.00$–7.02 and 7.05–7.10 would be ascribed to the aromatic protons of the alkylthiophene units and the thiophene units, respectively. The splitting patterns and intensity ratios of the peaks demonstrate that the isolated four oligothiophenes are identified with **1**, **2**, **3** and **4**, respectively. Furthermore, g.p.c. data summarized in *Table 1* suggest that the oligothiophenes are monodisperse and each average molecular weight

**Table 1** G.p.c. data and elemental analyses of hexyl-substituted oligothiophenes

| | | G.p.c. data[a] | | | Analyses (%) Found (calcd) | |
|---|---|---|---|---|---|---|
| Oligomer | *M* (calcd) | $M_n$ | $M_w$ | $M_n/M_w$ | C | H |
| **1** | 831 | 1.05 × $10^3$ | 1.10 × $10^3$ | 1.05 | 68.76 (69.34) | 7.52 (7.51) |
| **2** | 1246 | 1.55 × $10^3$ | 1.71 × $10^3$ | 1.10 | 69.12 (69.40) | 7.54 (7.44) |
| **3** | 1660 | 1.78 × $10^3$ | 1.97 × $10^3$ | 1.11 | 69.25 (69.43) | 7.48 (7.40) |
| **4** | 2075 | 2.27 × $10^3$ | 2.57 × $10^3$ | 1.13 | 68.96 (69.44) | 7.39 (7.38) |

[a] Number-average molecular weight ($M_n$) and weight-average molecular weight ($M_w$) were determined with polystyrene as a standard

estimated by g.p.c. is compatible with each one calculated. Elemental analyses of the oligothiophenes show that impurities such as bromides are negligible. These g.p.c. data and elemental analyses corroborate the identification of the oligothiophenes described above.

### *Neutral states*

The absorption spectra of the neutral hexyl-substituted oligothiophenes **1**, **2**, **3** and **4** in chloroform had $\pi$–$\pi^*$ transition bands at 3.02, 2.82, 2.77 and 2.73 eV, respectively. Poly(3-dodecylthiophene)[21,22] and poly(3-hexylthiophene)[23] which contained about 25 mol% head-to-head configuration had shown a $\pi$–$\pi^*$ transition band at 2.83 eV in chloroform. The value of the polymers is close to that of **2**, indicating those poly(3-alkylthiophene)s have a similar effective conjugation length to **2** (hexyl-substituted novithiophene). It can be presumed that the head-to-head configurations in the poly(alkylthiophene)s, existing at *ca.* eight ring intervals on average, largely twist the neutral polymer chains to restrict the conjugation length of the polymers.

### *One-electron oxidation*

The hexyl-substituted oligothiophenes **1**, **2**, **3** and **4** were oxidized with $FeCl_3$ in dichloromethane. It is generally admitted that two equivalents of $FeCl_3$ are necessary for one-electron oxidation of oligothiophenes[3,5]. The u.v.-vis.-n.i.r. absorption and the e.s.r. spectra of the hexyl-substituted oligothiophenes oxidized stoichiometrically were measured. *Figure 2* shows the u.v.-vis.-n.i.r. absorption spectra of the neutral and oxidized oligothiophenes **1**–**4** in solution. Each spectrum of the neutral oligothiophenes has a $\pi$–$\pi^*$ transition band at higher than 2.7 eV. When two equivalents of $FeCl_3$ are added to the oligothiophene solutions, the $\pi$–$\pi^*$ transition band disappears or reduces and two strong bands at about 1.5 eV and lower than 1.0 eV with a shoulder or a tailing on the high-energy side appear. The subsequent addition of $FeCl_3$ to the mixture leads to new absorption bands in the spectra of the oligothiophenes. These observations indicate that the first oxidation of the oligothiophenes is one-electron oxidation and generates cation radicals (polarons) as reported by Fichou *et al.* and other workers[9–14]. Furthermore, the addition of two equivalents of $FeCl_3$ to each neutral solutions resulted in the appearance of the intense e.s.r. signal ($\Delta H_{pp} = 4$–$6$) centred at $g = 2.003$ with no hyperfine structure. The numbers of spins per molecule of **1**, **2**, **3** and **4** derived from spin concentrations are approximately 0.8, 0.75, 0.7 and 0.6, respectively (*Figure 3*). The intensity of these e.s.r. signals grows apparently until two equivalents of $FeCl_3$ are added to the oligothiophene solutions. These low values of spins for the oligothiophenes (less than 1.0) would be

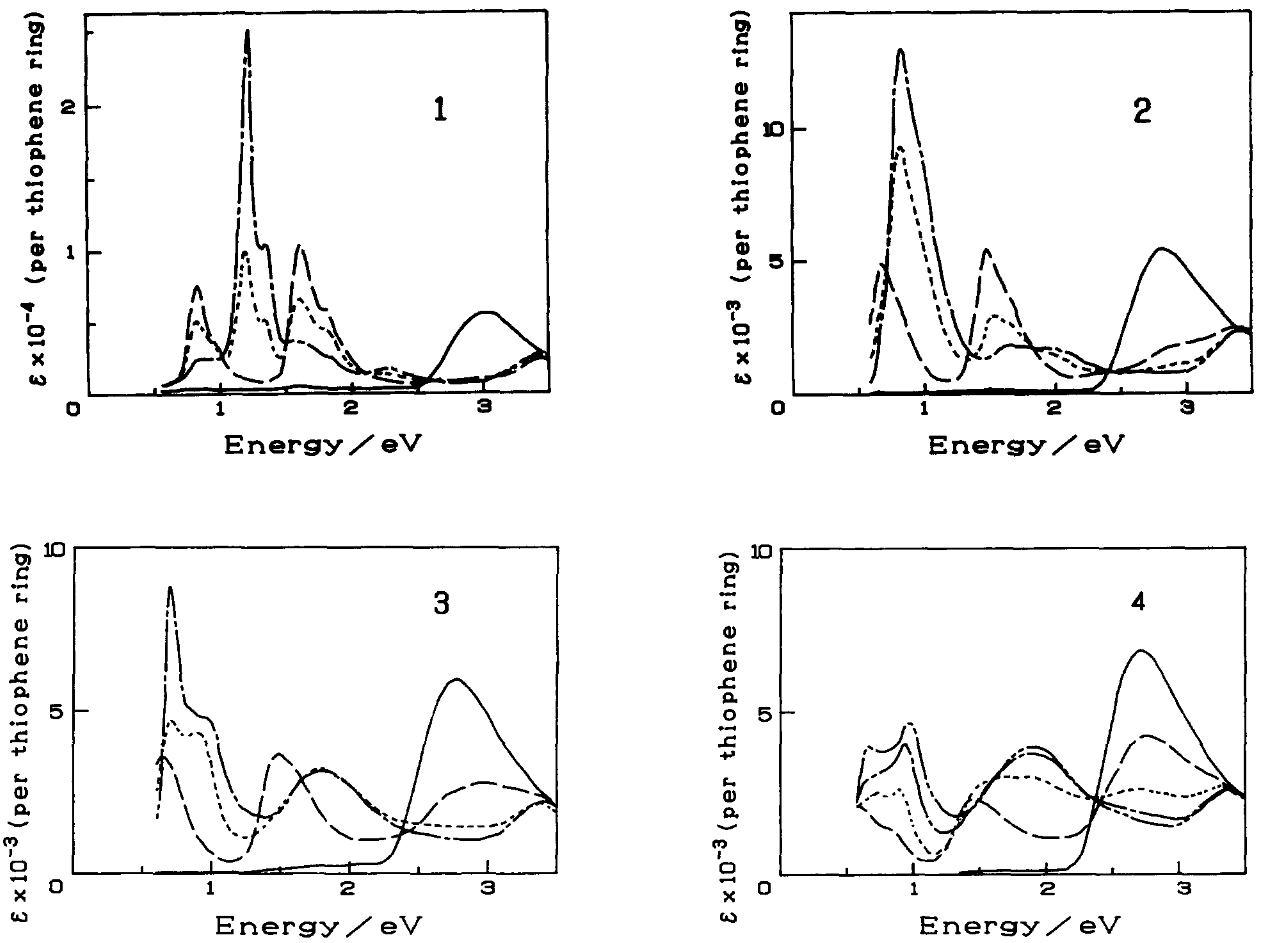

Figure 2 U.v.-vis.-n.i.r. absorption spectra of neutral and oxidized hexyl-substituted oligothiophenes **1**–**4**; neutral solutions (——), solutions oxidized with two equivalents of $FeCl_3$ (– – –), with four equivalents of $FeCl_3$ (- - - -), with six equivalents of $FeCl_3$ (– - –), with eight equivalents of $FeCl_3$ (– - - –)

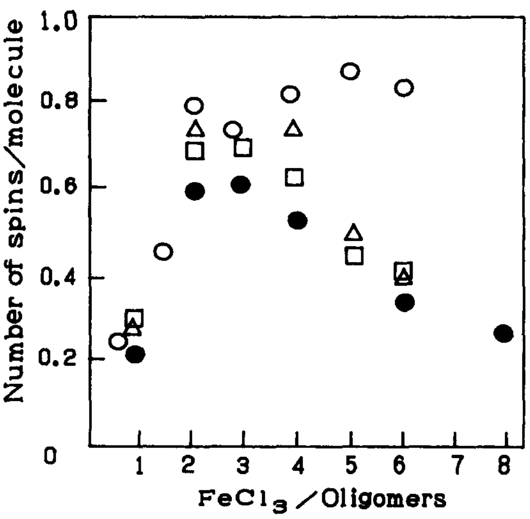

**Figure 3** Number of spins per molecular of hexyl-substituted oligothiophenes **1**–**4** against the amount of $FeCl_3$ added: **1** (○), **2** (△), **3** (□), **4** (●). The parameter '$FeCl_3$/oligomers' represents the mole ratio of $FeCl_3$ to oligomers

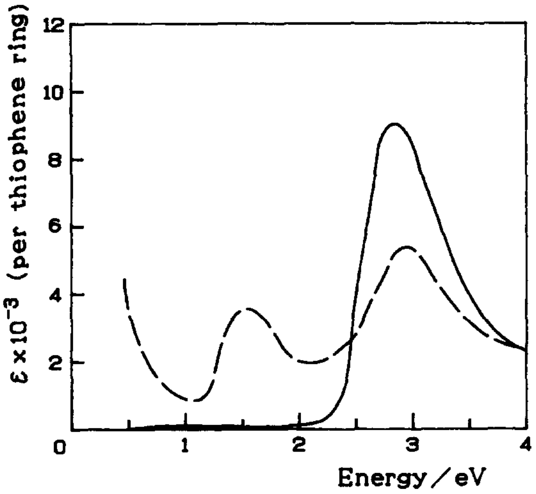

**Figure 4** Absorption spectra of poly(3-dodecylthiophene): neutral solution (—), oxidized solution (- -)

interpreted by formation of diamagnetic $\pi$-dimers of the cation radicals, which the shoulders and the tailing of the two absorption bands related to cation radicals in the spectra of the oligothiophenes imply[12] (*Figure 2*, dashed line). These e.s.r. data support the conclusion indicated for the absorption data.

With the addition of two equivalents of $FeCl_3$, the $\pi$–$\pi^*$ transition band of **1** vanishes, whereas the transition bands of **2**, **3** and **4** remain (*Figure 2*, dashed line). These show that the single cation radicals formed in the oligothiophene chain spread over the thiophene rings between 6 and 8.

Moreover, these absorption spectra of the one-electron oxidized oligothiophenes are similar to those of oxidized (doped) poly(3-dodecylthiophene) in solution[21,22] (*Figures 2* and *4*, dashed line) and poly(3-hexylthiophene) oxidized with $NOPF_6$ in solution[23]. In particular, the spectra of one-electron oxidized **4** are almost the same as those of oxidized poly(alkylthiophene)s. The energies of the bands related to the oxidized species in the poly(alkylthiophene)s (1.55–1.5 eV and 0.5– <0.5 eV) are, as well as the shapes of the spectra, similar to those related to cation radicals in the oligothiophenes (1.59–1.45 eV and 0.85– <0.5 eV). The two absorption bands at lower than 2 eV in spectra of the poly(alkylthiophene)s oxidized in solution had been attributed to dication (bipolaron) states from analogy with polythiophene films[21–23]. The observations described above lead us to speculate that oxidized species of the poly(alkylthiophene)s are also cation radicals.

### *Plural-electron oxidation*

For absorption and e.s.r. spectroscopy of the heavily oxidized hexyl-substituted oligothiophenes, **1** was oxidized with four and six equivalents of $FeCl_3$ and **2**, **3** and **4** were oxidized until the $\pi$–$\pi^*$ transition bands completely disappeared. Further addition of $FeCl_3$ to the cation radical solutions of **1**, **2**, **3** and **4** causes new absorption bands at (1.2, 1.3 and 2.3 eV), (0.8 and 2.1 eV), (0.7, 0.9 and 1.8 eV) and (0.7, 0.9 and 1.9 eV), respectively (*Figure 2*: dotted, dot-dashed and dot-dot-dashed line). These bands would be attributed to plural-electron oxidized species such as dication (bipolaron), trication radical or poly(cation radical). The intensity profiles of the new absorption bands are quite different from those of the bands lower than 2 eV observed in the oxidized poly(alkylthiophene) solutions (*Figure 4*: dashed line). In addition, the energies of the bands in the heavily oxidized oligothiophenes are not in accord with those in the oxidized poly(alkylthiophene)s. These results support the above-mentioned speculation that oxidized species of the poly(alkylthiophene)s are cation radicals.

In absorption spectra of the heavily oxidized oligothiophenes **1**, **2** and **3**, the new absorption bands grow and the intensity of the bands ascribed to the cation radicals decreases as $FeCl_3$ is added incrementally. In contrast, the absorption spectra of **4** oxidized with four equivalents of $FeCl_3$ show superposition of the bands attributable to the cation radicals generated by the first oxidation and the new bands appeared by the second oxidation. These observations indicate that heavily oxidized species in **1**, **2** and **3** are derived from the cation radicals to be dications (bipolarons), trication radicals, etc., whereas the cation radicals that occurred with the first oxidation of **4** would remain up to the second oxidation.

Further addition of $FeCl_3$ (three equivalents or above) led to no alteration of the $g$ and the $\Delta H_{pp}$ values of the e.s.r. signal observed in the first-oxidized oligothiophenes. The number of spins per molecule of **1** remain steady within experimental error in heavily oxidized states (*Figure 3*). The numbers of **2**, **3** and **4** reach a maximum with the addition of two to four equivalents of $FeCl_3$ and gradually decline to 0.4 at six equivalents, 0.4 at six equivalents, and 0.3 at eight equivalents, respectively. These considerable numbers of spins show the presence of radical species in the heavily oxidized oligothiophenes. This conclusion is inconsistent with reports on the oxidation of oligothiophenes in some papers[9–14]. However, one of those papers showed similar results of e.s.r. to those observed by us[11].

Furthermore, the appearance of the absorption bands attributable to free $FeCl_3$ (at 3.54 and 4.76 eV) was hardly observed in the spectra of the oxidized oligothiophene solutions (*Figure 2*), suggesting that all $FeCl_3$ was consumed for oxidizing the oligothiophenes.

## CONCLUSIONS

Four hexyl-substituted oligothiophenes with six to 15 thiophene units were prepared by a convenient method and oxidized chemically in solution. The absorption spectra of the oligothiophenes were compared with those of poly(alkylthiophene)s in detail. It was concluded that the neutral poly(alkylthiophene)s have a similar effective conjugation length to the hexyl-substituted novithiophene and the absorption bands lower than 2 eV observed in the oxidized poly(alkylthiophene) solutions are ascribed to cation radicals (polarons). The cation radical species generated by the first oxidation of the oligothiophenes have a limited delocalization length involving six to eight thiophene rings. In the second-oxidized states of the quindecithiophene derivative, the cation radical would exist in the chain.

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