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## Charge transport in liquid crystal network of terthiophene-siloxane block molecules†

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**In their thermotropic liquid-crystalline state, molecular semiconductors can show charge transport with high carrier mobility. Polymerization of the corresponding mesogens into a cross-linked network often deteriorates the charge transport. Here, we report that mesogens consisting of a terthiophene core and discrete oligodimethylsiloxane side-chains terminated by acrylate units can be photopolymerized in the columnar phase with retention of nanoscale order and charge transport capabilities. We argue that the strong tendency for microphase segregation protects the semiconducting block from reacting with free radicals during polymerization. This work provides new insights into the design of electroactive materials with charge transport properties.**

Organic electronics are actively pursued for application in stretchable conductors, semiconductors, and E-skin.<sup>1,2</sup> In comparison with traditional crystalline semiconductors, polymeric and molecular charge transporting materials are more flexible.<sup>3–5</sup> Yet this advantageous mechanical property is often accompanied by less favorable charge transport characteristics. The large number of conformations and intermolecular arrangements that molecules can adopt promotes flexibility and as a result this structural disorder tends to localize and induce trapping sites for charge carriers. To avoid this, one would like to decouple the mechanical from the electronic functionality of the material. Liquid-crystalline networks (LCNs) made of mesogens with  $\pi$ -conjugated, charge transporting cores and flexible polymerizable end-groups offer such an opportunity. These LC materials have been exploited to make an organic field-effect transistor

(OFET),<sup>6–8</sup> as spontaneous molecular order at the nanoscale promotes charge carrier mobility.<sup>9,10</sup> While the photopolymerized end-groups provide structural integrity and mechanical stiffness. However, it remains a challenge to make such LCNs for charge transport<sup>11</sup> because the polymerization step can change the molecular packing.<sup>12–15</sup> An additional difficulty is that intermediates in the polymerization reaction, *e.g.* free radicals, may attack the  $\pi$ -electron system of the mesogens leading to deep traps that impair charge transport.

Recently, materials combining the molecular directionality of liquid crystals (LCs) with the phase segregation of block copolymers have been explored. Early examples are phase-segregated LCs,<sup>16,17</sup> while more recent examples are based on discrete length block co-oligomers with one block consisting of discrete oligodimethylsiloxane (oDMS).<sup>18–23</sup> These materials assemble into well-defined phase-segregated structures with sub-10 nm feature sizes. The discrete nature of both the siloxanes and the complementary block promotes phase separation.<sup>24</sup> Hence, we envision using this design to accomplish nanophase segregation in LCNs such that the charge transport functionality carried by the semiconducting moiety is separated in space from the photopolymerizable functionality buried in the siloxane part. Therefore, chemical reactions of reactive species involved in the photopolymerization process on the delicate, unsaturated  $\pi$ -electron system of the semiconducting block may be prevented. Furthermore, after photopolymerization, the phase separation may prevent charge carriers injected into the semiconducting block from getting trapped at potential trap sites posed by unreacted polymerizable groups or remnants of photoinitiator. In addition, the flexible, liquid-like nature of the siloxane units may allow for enough mechanical flexibility such that the molecular packing of the semiconducting block is not impacted by strain that may have built up during the photopolymerization.

Here, we study the network formation and charge transport in phase-segregated LC **RM-TTPSi<sub>3</sub>** (Fig. 1). The mesogen is composed of a terthiophene central core decorated with short siloxane tails and terminated with polymerizable acrylate units.

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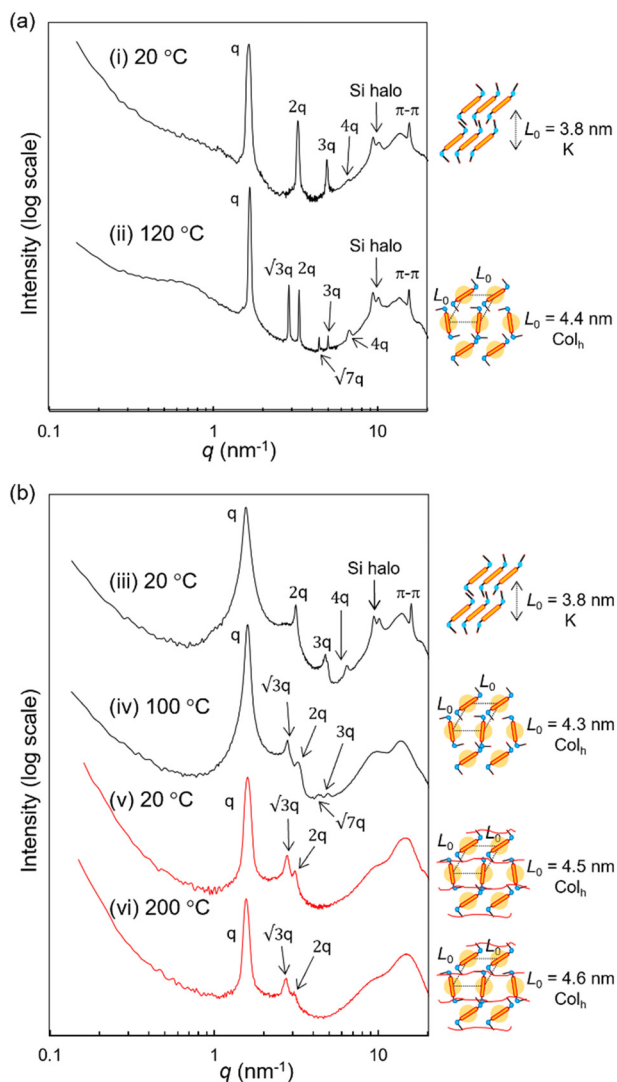
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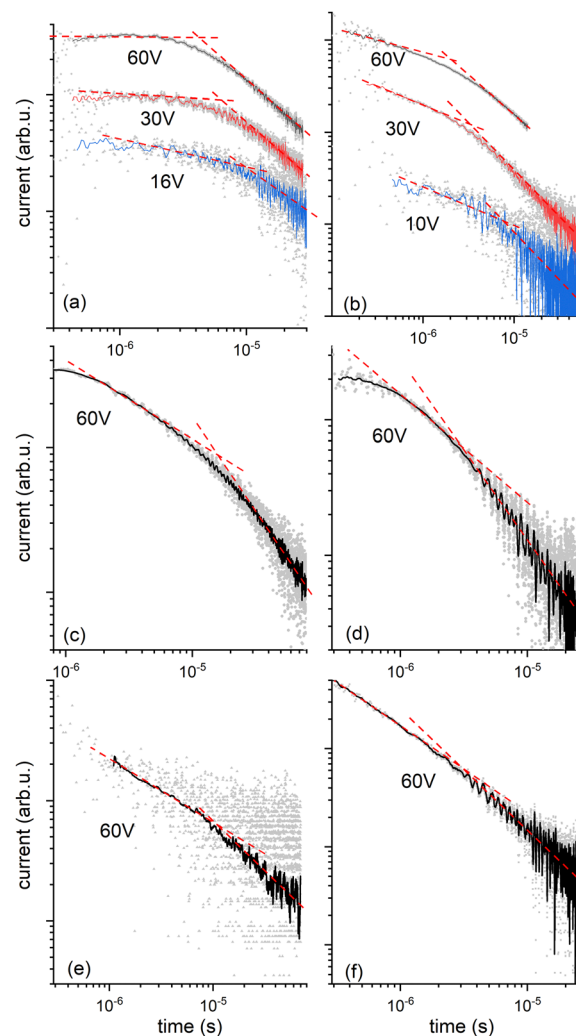




**Fig. 3** 1D transmission scattering profiles of (a) **HO-TTPSi<sub>3</sub>** and (b) **RM-TTPSi<sub>3</sub>** and schematic representations of the molecular packing. The black and red lines indicate a bulk and a film after photo-polymerization at 90 °C, respectively. The SAXS measurements were carried out at (i) 20 °C, (ii) 120 °C, (iii) 20 °C, (iv) 100 °C, (v) 20 °C and (vi) 200 °C.

illumination, its contribution to the overall photocurrent ends. The slow decay of the photocurrent over time observed for the bulk sample implies a broad distribution of transit times for individual carriers, *i.e.* dispersive transport. Nevertheless, at high temperatures ( $T = 130$  °C), a characteristic time for transport can be obtained from the kink in the photocurrent when plotted using logarithmic axes.

For compound **HO-TTPSi<sub>3</sub>**, almost nondispersive transport of holes is observed in the Col<sub>h</sub> phase ( $T = 130$  °C, Fig. 4a and Table 1) with a mobility of  $2 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. This value for hole mobility in an LC phase is comparable to mobilities reported for alkyl-functionalized terthiophenes in their LC state.<sup>25–29</sup> Preliminary measurements of hole transport at room temperature in the crystalline phase indicate that the charge transport characteristics of the Col<sub>h</sub> phase are largely



**Fig. 4** Transient photocurrent curves in time-of-flight mobility measurements. (a) Hole current in **HO-TTPSi<sub>3</sub>** in the Col<sub>h</sub> phase at 130 °C, for various applied bias voltages. The sample thickness is 20 μm in all cases shown here. (b) Electron current of **HO-TTPSi<sub>3</sub>** in the Col<sub>h</sub> phase at 130 °C. (c) Hole current of **RM-TTPSi<sub>3</sub>** polymerized at 90 °C. (d) Electron current of **RM-TTPSi<sub>3</sub>** polymerized at 90 °C. (e) Hole current of **RM-TTPSi<sub>3</sub>** polymerized at 50 °C. (f) Electron current of **RM-TTPSi<sub>3</sub>** polymerized at 50 °C. (c–f) Measurements conditions: 140 °C and applied bias 60V.

**Table 1** Summary of **HO-TTPSi<sub>3</sub>** and photopolymerized **RM-TTPSi<sub>3</sub>** mobilities

Material	$T_{\text{pol}}^a$ [°C]	$T_{\text{meas}}^b$ [°C]	$\mu_{\text{hole}}^c$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	$\mu_{\text{electron}}^c$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]
<b>HO-TTPSi<sub>3</sub></b>	—	130	$2 \times 10^{-2}$	$3 \times 10^{-2}$
<b>HO-TTPSi<sub>3</sub></b>	—	30	$2 \times 10^{-2}$	Dispersive
<b>RM-TTPSi<sub>3</sub></b> <sup>c</sup>	90	140	$4 \times 10^{-3}$	$2 \times 10^{-2}$
<b>RM-TTPSi<sub>3</sub></b> <sup>c</sup>	90	100	$1 \times 10^{-3}$	$1 \times 10^{-2}$
<b>RM-TTPSi<sub>3</sub></b> <sup>c</sup>	50	140	$5 \times 10^{-3}$	$2 \times 10^{-2}$

<sup>a</sup> Temperature at which photopolymerization was performed. <sup>b</sup> Temperature of the photocurrent transient measurement. <sup>c</sup> Polymerized.

maintained in the crystalline phase (Table 1). Transport of electrons is clearly dispersive, yet average mobilities for electrons at high temperatures are similar to those for holes



