## Functional Disubstituted Polyacetylenes and Soluble Cross-Linked Polyenes: Effects of Pendant Groups or Side Chains on Liquid Crystallinity and Light Emission of Poly(1-phenyl-1-undecyne)s

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ABSTRACT: A group of new poly(1-phenyl-1-undecyne)s with different mesogenic and chromophoric pendant groups or side chains were successfully synthesized and the structural variations were found to greatly affect the mesomorphic and luminescent properties of the polymers. The 1-phenyl-1-undecyne monomers  $(C_{6}H_{5})C \equiv C(CH_{2})_{9}OCOR$  with  $R = C_{6}H_{4} - C_{6}H_{10} - C_{5}H_{11}$  (1),  $C_{6}H_{4} - OCO - C_{6}H_{4} - OC_{6}H_{13}$  (2), and  $C_{6}H_{4}-C \equiv C-C_{6}H_{4}-OC_{7}H_{15}$  (3) were prepared by simple esterification and/or coupling reactions. The polymerizations of 1-3 were effected by WCl<sub>6</sub>-Ph<sub>4</sub>Sn in toluene at 60-80 °C, giving polymers with high molecular weights in good isolation yields. The structures and properties of the polymers were characterized and evaluated by GPC, IR, NMR, TGA, DSC, POM, XRD, UV, and PL analyses. The polymerizations of 1 and 2 yield linear poly(1-phenyl-1-alkyne)s P1 and P2, respectively, while that of 3 gives a nonlinear macromolecule with its poly(1-phenyl-1-alkyne) main chain cross-linked by the oligo-(diphenylacetylene) side chains resulted from the partial polymerization of its diphenylacetylene pendants (P3x). All the polymers are completely soluble in common solvents and are thermally stable with  $T_{\rm d}$   $\geq$  390 °C. Polymers P1 and P2 undergo nematic and smectic transitions at ~100 and ~170 °C, respectively, while P3x is nonmesomorphic. Upon excitation, the poly(1-phenyl-1-alkyne) chains of P1 and P2 emit a strong blue light of 460 nm, with their fluorescence quantum efficiencies comparable to or higher than that of poly(1-phenyl-1-octyne), a highly emissive disubstituted polyacetylene. Polymer P3xemits a blue-green light of 490 nm, due to the energy transfer from its poly(1-phenyl-1-octyne) main chain to its oligo(diphenylacetylene) side chains.

#### Introduction

Polyacetylene  $-(HC=CH)_n$  is well-known as an electroactive polymer<sup>1</sup> but is also notorious for its instability and intractability.<sup>2</sup> Replacements of one or two hydrogen atoms in the repeat unit of the polymer by one or two substituents give rise to mono-  $\{-[(R)C=$  $CH]_n$  or disubstituted polyacetylenes {-[(R)C=  $C(R')]_n$ , respectively, which can be stable and processable, provided that the  $R^{(\prime)}$  groups are properly chosen.<sup>3,4</sup> Compared to its monosubstituted counterpart, a disubstituted polyacetylene often enjoys such advantages as being thermally more stable, better film forming, and mechanically much stronger.<sup>5,6</sup> Although polyacetylene itself is not luminescent,<sup>7</sup> recent investigations have revealed that its substituted derivatives can be emissive,<sup>5,8,9</sup> with disubstituted polyacetylenes being generally more luminescent than their monosubstituted counterparts.<sup>10,11</sup> Among disubstituted polyacetylenes, poly(1-phenyl-1-alkyne)s (PPAs) [e.g., poly(1-phenyl-1-octvne) (PPO)]and poly(diphenylacetylene)s (PDPAs) [e.g., poly(1-{p-[(1-naphthyloxy)octyloxy]}-

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phenyl-2-phenylacetylene) (PNOPPA)] (Chart 1) are two typical examples of highly luminescent polyacetylenes. Both polymers can emit efficiently, but the colors of their emissions are different: the light emitted from the former is blue while that from the latter is green.<sup>12,13</sup>

We have been particularly interested in the blue lightemitting PPA and have synthesized a variety of its derivatives with an aim of further enhancing its emission efficiency as well as endowing it with new functionality.<sup>5,14</sup> In our previous work, we prepared a series of new PPAs, in which chromophoric and mesogenic biphenyl cores were attached to the polyene backbone as pendants through alkyl spacers of different chain lengths (m; Chart 2).<sup>15</sup> The chain length was found to greatly affect the properties of the biphenyl-containing PPAs: for example, the polymer with the shorter chain length (m = 4) was not liquid crystalline, whereas that with the longer chain (m = 9) packed into a smectic A (SmA) mesophase in a monolayer arrangement. Both of the polymers emitted a blue light of 460 nm, but the fluorescence quantum yield  $(\Phi_F)$  of the polymer with the longer spacer was higher than that of the one with the shorter spacer.

Since the long spacer is good for the mesomorphism and luminescence of PPAs, in this work, we synthesized a group of 1-phenyl-1-alkyne monomers with nine methylene spacers, namely, 1-phenyl-1-undecynes, containing different mesogenic or chromophoric cores (1-3); Scheme 1). Compared with the biphenyl core in

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the polymers shown in Chart 2, the phenylcyclohexane core in 1 is less conjugated and the phenyl benzoate core in 2 is more polarized, while the diphenylacetylene core in 3 is, on the other hand, more conjugated. In this paper, we demonstrate that the variation in the core structure greatly affects the polymerization behaviors of the monomers as well as the physical properties of the resultant polymers. Thus, monomers 1 and 2 are polymerized into linear PPA chains of P1 and P2, respectively, whereas a linear PPA of P3 is not yielded by the polymerization of monomer **3**; instead, a nonlinear polyacetylene with a PPA backbone and oligo-(diphenylacetylene) (ODPA) pendants (P3x) is obtained (Chart 3). The linear polyacetylene bearing the phenylcyclohexane- (P1) and phenyl benzoate-cored pendants (P2) are nematogenic and smectogenic, respectively, but the nonlinear, cross-linked polyene with the diphenylacetylene-cored pendants and ODPA branches (P3x) are completely nonmesomorphic. Furthermore, P1 and P2 are blue emitters, while P3x emits a blue-green light.

### **Results and Discussion**

**Monomer Preparations and Polymer Syntheses.** 1-Phenyl-1-undecyne monomers 1 and 2 were prepared by single-step, room-temperature esterifications of 11-phenyl-10-undecyn-1-ol (4)<sup>15</sup> with 4-(4-pentylcyclohexyl)benzoic acid (5) and 4-(4-hexyloxyphenylcarbonyloxy)benzoic acid (6), respectively, in the presence of a mixture of 1,3-dicyclohexylcarbodiimine (DCC), *p*-toluenesulfonic acid (TsOH), and 4-(dimethylamino)pyridine (DMAP; Scheme 1). Monomer 3 was prepared by esterification of 4-ethynylbenzoic acid (7) with 11-phenyl-10-undecyn-1-ol (4) in the presence of a mixture of DCC, TsOH, and DMAP, followed by the coupling of the resultant diyne (8) with 4-heptyloxyiodobenzene (9) catalyzed by a palladium complex. All of the monomers were isolated in good yields ( $\sim$ 56–90%) after purification by column chromatography and recrystallization. The monomers were characterized by spectroscopic methods, from which satisfactory analysis data were obtained (see Experimental Section for details). While 1 is a colorless liquid, 2 and 3 are white solids but do not exhibit liquid crystallinity at elevated temperatures.

We tried to polymerize the nonmesomorphic monomers in the hope that polymerization will enable the mesogenic pendants to enter the liquid crystalline state.<sup>16,17</sup> In our previous work, we found that WCl<sub>6</sub>-Ph<sub>4</sub>Sn effected the polymerizations of the biphenylcontaining 1-phenyl-1-alkynes.<sup>15</sup> Polymerization of 1 using the same catalyst was thus attempted. Although the reaction carried out at room temperature fails to produce any polymer, the polymerization performed at 60 °C gives a yellow powdery product, which is isolated in  $\sim 69\%$  yield by precipitation of its toluene solution into acetone (Table 1, no. 2). Increasing the temperature to 80 °C did not affect the polymerization result much. The monomer does not undergo polymerization in the presence of MoCl<sub>5</sub>-Ph<sub>4</sub>Sn. Mixtures of NbCl<sub>5</sub>- and TaCl<sub>5</sub>-Ph<sub>4</sub>Sn are the most widely used catalysts for the polymerizations of disubstituted acetylenes<sup>3,18</sup> but the reactions catalyzed by these mixtures give little or no polymeric products (Table 1, nos. 5 and 6), probably due to the poisoning interaction of the polar ester groups of 1 with the transition metal compounds. Monomer 2 is polymerized in a similar way. Although at room-temperature WCl<sub>6</sub>-Ph<sub>4</sub>Sn is again ineffective in polymerizing 2, the reactions conducted at elevated temperatures yield high molecular weight polymers. The polymer is isolated in an impressively high yield ( $\sim 86\%$ ) when the polymerization is carried out at 80 °C (Table 1, no. 9).

Similar to monomers 1 and 2, monomer 3 can also be readily polymerized into high molecular weight polymers by the W catalyst at high temperatures (Table 1, nos. 10 and 11), with the Mo, Nb, and Ta mixtures being again ineffective catalysts. However, different from the polymers of 1 and 2, those of 3 show multipeaked GPC chromatograms. As can be seen from Figure 1, the polymer obtained from the polymerization of 3 at 60 °C gives several peaks: one main peak in the "normal" molecular weight region and a few minor peaks in the very high molecular weight region. The high molecular weight fractions are increased when the polymerization temperature is increased to 80 °C.

The multipeaked GPC chromatograms suggest that both of 1-phenyl-1-alkyne and diphenylacetylene triple bonds of 3 have undergone polymerizations. The WCl<sub>6</sub>-Ph<sub>4</sub>Sn mixture is a good catalyst for the polymerizations of 1-phenyl-1-alkynes (e.g., 1 and 2), and the PPA chains formed by the polymerization of the 1-phenyl-1-alkyne triple bonds of 3 are thus believed to be the backbone of the polymer of **3**. Although it has been reported that the WCl<sub>6</sub>-Bu<sub>4</sub>Sn mixture is not a catalyst for the polymerizations of diphenylacetylenes,<sup>19</sup> the triple bonds of the diphenylacetylene pendants of the polymer of **3** may have been partially polymerized by WCl<sub>6</sub>-Ph<sub>4</sub>Sn, because our recent investigations found that this catalyst could polymerize diphenylacetylene derivates of  $C_6H_5C \equiv CC_6H_4O(CH_2)_mOAr$ , with Ar being naphthyl and carbazolyl groups.<sup>20</sup> The partial polymerization of diphenylacetylene triple bonds in the pendants of the polymer of 3 should result in the formation of cross-linked gels, which would normally be insoluble. The products of the polymerizations of **3** are, however, completely soluble in common solvents such as toluene, THF, and chloroform. The syntheses of soluble polymers with cross-linked molecular structures have been accomplished in certain polymerization systems under well-controlled conditions.<sup>21</sup> It is amazing that soluble, cross-linked polyacetylenes can be prepared under the normal conditions of acetylene polymerization.





**Structural Characterizations by Spectroscopic** Methods. Spectroscopic analyses readily confirm that the polymers of 1 and 2 are linear PPA chains bearing phenylcyclohexane- and phenyl benzoate-cored pendants, whose molecular structures can be respectively represented by P1 and P2 shown in Chart 3. Since the analysis of linear polyacetylene structures has been a routine job in our laboratories and has been reported in many of our previous papers,<sup>9,11,15</sup> the structural characterizations of P1 and P2 will not be discussed here in detail (their numeric spectroscopic data can, however, be readily found in Experimental Section). Our discussion will instead be focused on the spectroscopic verification of the nonlinear molecular structure of the polymer of **3** suggested by its GPC trace, that is, a macromolecule with a PPA backbone cross-linked by the ODPA branches resulted from the partial polymerization of its diphenylacetylene pendants (P3x).

Figure 2 shows the IR spectrum of P3x. For comparison, the spectrum of its monomer **3** is also given in the figure. The vibration band of C=C stretching of a 1-phenyl-1-alkyne is normally very weak and can only be occasionally observed at ~2230 cm<sup>-1</sup>,<sup>15,22</sup> while that of a diphenylacetylene is strong enough to be visible at ~2200 cm<sup>-1</sup>.<sup>19</sup> Monomer **3** exhibits a readily identifiable band at 2217 cm<sup>-1</sup>, which is clearly associated with the C=C stretching of its diphenylacetylene group. This absorption band is still observable in the spectrum of P3x, indicating that the polymer contains diphenylacetylene triple bonds in its molecular structure. This proves that the diphenylacetylene triple bonds have been only partially polymerized by the W-catalyzed acetylene polymerization.

Figure 3 shows the <sup>1</sup>H NMR spectra of P3x and its monomer **3**. The resonance peaks of the phenyl protons

of **3** at  $\delta$  7.39 and 7.25 shift upfield to  $\delta$  6.84 upon polymerization,<sup>22</sup> as observed in the case of polymerization of the biphenyl-containing 1-phenyl-1-alkynes (Chart 2).<sup>15</sup> The resonance of the protons of the methylene group directly linked to the triple bond ( $\equiv$ CCH<sub>2</sub> or propargyl protons) becomes very weak after polymerization (cf., panels A and B of Figure 3) because the allenic protons ( $\equiv$ CCH<sub>2</sub>) are attached to a rigid polymer backbone.<sup>5,6b,23,24</sup>

In the <sup>13</sup>C NMR spectrum of **3**, the carbon atoms of its 1-phenyl-1-alkyne triple bond resonate at  $\delta$  80.6 (*b*) and 90.3 (c), while those of its diphenylacetylene one are located at  $\delta$  92.6 (*i*) and 87.4 (*j*) (Figure 4A). After polymerization, the resonance peaks of the 1-phenyl-1alkyne triple bond disappear, and that of the propargyl carbon (*d*) downfield shits due to its transformation to allenic structure (Figure 4B). This confirms that the 1-phenyl-1-alkyne triple bonds of molecules of **3** have all been consumed by the acetylene polymerization. The resonance peaks of the diphenylacetylene triple bond (i and j), on the other hand, do not disappear but are weakened in intensity, spectroscopically proving that not all but part of the diphenylacetylene triple bonds of the molecules of 3 have been polymerized. The olefinic carbon atoms b and c of the PPA backbone and the ODPA branches resonate in a broad chemical shift range owing to the rigid nature of the polyacetylene chains.6b,22-24

Thermal Stability and Oxidative Resistance. The monosubstituted polyacetylenes such as poly(1-alkyne)s  $-\{HC=C[(CH_2)_mCH_3]\}_n$  are thermally unstable.<sup>5,6</sup> Poly-(1-hexyne) (PH), for example, starts to lose its weight at a temperature  $(T_d)$  as low as 150 °C (Figure 5). Thermal stability of the biphenyl-containing poly-(1-alkyne)s is much higher and their  $T_d$ 's move up to  ${\sim}300\ \rm ^\circ C.^{24,25}$  As shown in Figure 5, the PPA derivatives of P1, P2, and P3x are thermally very stable and their  $T_{\rm d}$ 's are as high as ~390 °C. Clearly, the resistance of the polyacetylenes to thermolytic decomposition is boosted by the replacement of the hydrogen atom in the repeat unit of a poly(1-alkyne) with a phenyl ring. It is worth noting that  $\sim 40\%$  of the original weight of P3x is left when it is pyrolyzed at 550 °C, at which almost all of the weights of P1 and P2 are lost. Thermally induced acetylene polymerization<sup>26</sup> of the triple bonds of the unpolymerized diphenylacetylene pendants of P3x further cross-links the polymer, and the resultant thermoset gel may have graphitized upon pyrolysis, resulting in the high weight residue at the high temperature.

To further evaluate the stability of the polymers, we checked the changes of their molecular weights with

(1 0)

Table 1. Polymerizations of 1-Phenyi-1-undecynes $(1-3)^{\alpha}$												
no.	catalyst	temp (°C)	yield (%)	$M_{ m w}{}^b$	$M_{ m w}\!/\!M_{ m n}{}^b$							
11-[4-(4-Pentylcyclohexyl)phenylcarbonyloxy]-1-phenyl-1-undecyne (1)												
1	$WCl_6-Ph_4Sn$	room temp $^{c}$	0									
2	$WCl_6-Ph_4Sn$	60	68.5	$62\ 400$	2.3							
3	$WCl_6-Ph_4Sn$	80	64.5	87 200	2.7							
4	$MoCl_5-Ph_4Sn$	60	0									
5	$NbCl_5-Ph_4Sn$	60	trace									
6	$TaCl_5-Ph_4Sn$	60	0									
	11-[4-(4-Hexvlo	xvphenvlcarbonvloxv)phen	vlcarbonvloxv]-1-phenv	l-1-undecvne ( <b>2</b> )								
7	$WCl_6-Ph_4Sn$	room temp <sup>c</sup>	0									
8	$WCl_6 - Ph_4Sn$	60	25.8	$44\ 100$	1.7							
9	$WCl_6-Ph_4Sn$	80	86.2	$36\ 100$	1.6							
	11-[4-(4-Hept	yloxyphenylethynyl)pheny	lcarbonyloxy]-1-phenyl-1	l-undecyne ( <b>3</b> )								
10	$WCl_6-Ph_4Sn$	60	32.2	$50 \ 500^{d}$	$1.7^d$							
11	$WCl_6-Ph_4Sn$	80	42.3	$57 \ 700^{d}$	$1.9^d$							
12	$MoCl_5-Ph_4Sn$	60	0									
13	$NbCl_5-Ph_4Sn$	60	trace									
14	$TaCl_5-Ph_4Sn$	60	0									

<sup>*a*</sup> Carried out under nitrogen in toluene for 24 h;  $[M]_0 = 0.2 \text{ M}$ ,  $[MtCl_x] = [Ph_4Sn] = 10 \text{ mM}$  (Mt = W, Mo, Nb, Ta; x = 5, 6). <sup>*b*</sup> Determined by gel permeation chromatograph (GPC) in THF on the basis of a polystyrene calibration. <sup>*c*</sup> Room temperature. <sup>*d*</sup> Values for the main peaks of the multipeaked GPC curves (cf., Figure 1).



**Figure 1.** GPC chromatograms of P3x prepared by  $WCl_6-Ph_4Sn$  in toluene at 60 °C and 80 °C.



**Figure 2.** IR spectra of (A) **3** and (B) its polymer P3x (sample taken from Table 1, no. 10).

time and temperature. GPC analyses of the polymer samples stored under ambient conditions in air for more than 4 years find no changes in their molecular weights, revealing that the polymers are very stable at room temperature. We annealed P1 in air for 2 h at different temperatures and plotted its  $M_w$  against the annealing temperature in Figure 6. Almost no change in  $M_w$  is observed when P1 is annealed at temperatures up to 150 °C, although further heating to 200 °C leads to a slight increase in  $M_w$ . This confirms that P1 is resistant



**Figure 3.** <sup>1</sup>H NMR spectra of chloroform-*d* solutions of (A) **3** and (B) its polymer P3x (sample taken from Table 1, no. 10). The solvent peak is marked with an asterisk (\*).

to thermolysis caused by oxidative chain scission. The high stability of the polymer is possibly due to the "jacket effect" of its pendant groups,<sup>5</sup> which sterically shields the polyene backbone from the thermolytic attack.

Nematic and Smectic Mesomorphisms. To know whether the 1-phenyl-1-alkyne derivatives become liquid crystalline after polymerization, we studied thermal transitions of their polymers by differential scanning calorimeter (DSC). Disappointedly, no liquid crystalline transitions are detected by DSC for P3x in either heating or cooling cycle. This is probably caused by its nonlinear, irregularly cross-linked structure, in which the ODPA branches segregate the unpolymerized diphenylacetylene mesogens in a random fashion. Delightfully, however, linear polymers P1 and P2 both exhibit liquid crystallinity, as indicated by their DSC



**Figure 4.** <sup>13</sup>C NMR spectra of chloroform-*d* solutions of (A) **3** and (B) its polymer P**3**x (sample taken from Table 1, no. 10). The solvent peaks are marked with asterisks (\*).

thermograms (Figure 7). In the first cooling cycle of P1, an exothermic peak associated with its i-n transition is observed at 108.4 °C. Its corresponding n-i transition is detected as a broad endothermic bump peaked at 95.0 °C during the second heating scan. The nematic phase is thus enantiotropic. Polymer P2 displays a better-ordered SmA phase at 168.3 °C in the first cooling cycle. The mesophase is again enantiotropic with the corresponding SmA-i transition observed at 169.2 °C in the second heating scan.

When the isotropic liquid of P1 is cooled, typical Schlieren textures are formed. An example of the polarized optical microscope (POM) photographs of the Schlieren textures is given in Figure 8A, where four brushes radiate from a disclination point. The polymer also displays Schlieren texture containing a singularity with two brushes or  $s = \pm 1/2$  (data not shown). Since disclination with  $s = \pm 1/2$  is incompatible with SmC phase, the Schlieren textures thus should be associated



**Figure 5.** Thermogravimetric analysis (TGA) thermograms of P1 (sample taken from Table 1, no. 2), P2 (Table 1, no. 8), P3x (Table 1, no. 10), and poly(1-hexyne) (PH)<sup>6b</sup> recorded under nitrogen at a heating rate of 20 °C/min.



**Figure 6.** Effect of temperature on the molecular weight  $(M_w)$  of P1 (sample taken from Table 1, no. 2). The polymer samples were annealed in air at given temperatures for 2 h.

with the nematic phase of P1.<sup>27</sup> It is noted that all of the monosubstituted polyacetylenes bearing the similar mesogenic pendants prepared so far exhibit SmA phases.<sup>28</sup> The formation of the nematic phase in P1 is probably caused by its more rigid disubstituted polyacetylene backbone, which hampers its mesogenic pendants from packing into SmA phase. Compared to the phenylcyclohexane mesogens in P1, the phenyl benzoate mesogens in P2 have a stronger tendency to enter into an SmA phase.<sup>17a,29</sup> Thanks to this propensity for smecticity, bâtonnets, indicative of the formation of SmA phase, are observed when the isotropic liquid of P2 is cooled. The bâtonnets could readily grow into the focalconic fan textures of SmA phases in the monosubstituted polyacetylene systems<sup>17a,29,30</sup> but are difficult to develop into the typical SmA texture in P2 (Figure 6B), again due to the rigidity of its PPA backbone.

Table 2 summarizes the thermal transitions of P1 and P2 as well as their corresponding enthalpy and entropy changes. The small changes in  $\Delta H$  (< |0.7| kJ/mru) and  $\Delta S$  [< |1.7| J/(mru K)] involved in the mesophase transitions of P1 suggest a poor ordering of its phenyl-cyclohexane-cored mesogenic units and support the assignment of nematicity to its Schlieren textures.<sup>31</sup> The



**Figure 7.** DSC thermograms of mesomorphic PPA derivatives of (A) P1 (sample taken from Table 1. no. 2) and (B) P2 (Table 1, no. 8) recorded under nitrogen during the first cooling and second heating scans at a scan rate of 10 °C/min.

mesomorphic transitions of P2, however, involve bigger changes in  $\Delta H$  and  $\Delta S$  [up to  $\sim 12$  kJ/mru and  $\sim 27$  J/(mru K), respectively], in agreement with the smecticity of its mesophase revealed by the POM observation.

We carried out X-ray diffraction (XRD) experiments with the aim of further verifying the mesophase assignments and gaining insights into the packing arrangements of the mesogens in the polymers. It is known that a typical XRD diffractogram of a nematic liquid crystal is characterized by a diffuse halo and broad bumps in the high- and low-angle regions, respectively.<sup>31</sup> As can be seen from Figure 9, the diffractogram of the sample of P1 rapidly quenched from 100 °C by liquid nitrogen possess these two features, thus substantiating the nematicity assignment to its mesophase at this temperature. Polymer P2, however, shows not only a diffuse halo in the high-angle region but also Bragg reflection peaks in the low-angle region. The sharp reflection at  $2\theta = 2.65^{\circ}$  corresponds to a layer spacing of 33.31 Å, close to the molecular length for the repeat unit of P2 at its most extended conformation (l = 35.52 Å). Its mesogens are thus packed in a monolayer fashion. The high-order secondary reflection at  $2\theta = 5.25^{\circ}$ (d = 16.82 Å) is readily detected by the XRD diffratometer, indicative of good packing arrangements in this liquid crystal system. The reflection at  $2\theta = 7.7^{\circ}$  (d = 11.47 Å) may be associated with the packing of the appendages without the flexible tails.

Electronic Absorption and Light Emission. The absorption spectra of the polymer solutions in THF are shown in Figure 10. The mesogenic pendants of P1 and P2 absorb at ~240 and ~264 nm with molar absorptivities ( $\epsilon$ ) of ~18630 and ~22150 mol<sup>-1</sup> L cm<sup>-1</sup>, respectively. The UV spectrum of P1 exhibits a broad



**Figure 8.** Mesomorphic textures observed on cooling (A) P1 (sample taken from Table 1, no. 2) to 100 °C and (B) P2 (Table 1, no. 8) to 160 °C from their isotropic melts. Scale bar: 20  $\mu$ m.

bump at ~332 nm with an  $\epsilon$  of ~2550 mol<sup>-1</sup> L cm<sup>-1</sup>, which is assigned to the absorption of its PPA backbone. This assignment is supported by the observation that poly(1-phenyl-1-nonyne), a parent form of P1, absorbs at a similar wavelength ( $\lambda$  ~325 nm) with a similar absorptivity ( $\epsilon$  ~3000 mol<sup>-1</sup> L cm<sup>-1</sup>).<sup>32</sup> This is further attested by the overlapping of the absorption spectrum of P1 with that of PPO, another parent form of P1, in the wavelength range ~300–350 nm. The PPA backbone of P2 shows similar absorption behaviors in the similar spectral region ( $\lambda$  ~ 330 nm,  $\epsilon$  ~ 2110 mol<sup>-1</sup> L cm<sup>-1</sup>).

The absorption spectrum of P3x is, however, different from those of P1 and P2. The chromophoric pendant of P3x absorbs at  $\sim$ 316 nm. This absorption is strong  $(\epsilon \sim 25120 \text{ mol}^{-1} \text{ L cm}^{-1})$ , owing to the molecular polarization induced by the push-pull interaction exerted on the chromophore by the electron-donating ether group (-O-) and electron-withdrawing ester group  $(-CO_2-)$  attached to the two ends of the diphenylacetylene core. The appearance of this strong absorption peak confirms that P3x bears the diphenvlacetylene pendants, or in other words, not all of the diphenylacetylene triple bonds have been polymerized by the W-catalyzed acetylene polymerization. Because of the overlapping with this strong pendant absorption peak, the absorption peak of the PPA backbone of P3x now appears as a shoulder at  $\sim$ 332 nm with an apparent absorptivity of  $\sim 21980 \text{ mol}^{-1} \text{ L cm}^{-1}$ .

Absorption spectrum of a PDPA chain is characterized by its absorptions in the longer wavelength region  $(\lambda > 400 \text{ nm})$ ,<sup>19</sup> where a PPA chain does not absorb. For example, PNOPPA, a PDPA derivative, absorbs at  $\lambda > 400 \text{ nm}$ , with absorption peak at ~425 nm

					0	0				
				$T$ , °C [ $\Delta H$ , kJ/mru; $\Delta S$ , J/(mru K)] <sup>c</sup> (by DSC) <sup>a</sup>						
no	0.	polymer		cooling scan			heating scan			
$\frac{1}{2}$		P1 P2		i 108.4 (-0.63; -1.64) n i 168.3 (-7.58; -17.18) SmA			n 95.0 (0.40; 1.35) i SmA 169.2 (11.78; 26.65) i			
				molecular packing arrangements (by XRD)						
no.	polymer	$T(^{\circ}\mathrm{C})^{b}$	$d_1$ (Å)	$d_2({ m \AA})$	$d_3$ (Å)	$d_4({ m \AA})$	$l$ (Å) $^d$	ratio $d_1/l$	phase	
$\frac{3}{4}$	P <b>1</b> P <b>2</b>	$\begin{array}{c} 100 \\ 155 \end{array}$	33.31	16.82	11.47	$4.36 \\ 4.39$	$29.90 \\ 35.52$	0.94	n SmA	

Table 2. Thermal Transitions and Packing Arrangements of P1 and P2

<sup>*a*</sup> Data taken from the DSC thermograms recorded under nitrogen in the first cooling and second heating scans; abbreviations: n = nematic phase, SmA = smectic A phase, and i = isotropic liquid. <sup>*b*</sup> The mesomorphic structure in the liquid crystalline phase at the given temperature was frozen by the rapid quenching with liquid nitrogen. <sup>*c*</sup> Abbreviation: mru = monomer repeat unit. <sup>*d*</sup> Molecular length (*l*) calculated from the monomer repeat units in their fully extended conformation.



**Figure 9.** X-ray diffraction patterns of mesomorphic PPA derivatives quenched by liquid nitrogen from their liquid crystalline states: P1 (sample taken from Table 1, no. 2) at 100 °C and P2 (Table 2, no. 8) at 155 °C.

 $(\epsilon \sim 3000 \text{ mol}^{-1} \text{ L cm}^{-1})$ . No absorption peak is, however, observed at this wavelength in the spectrum of P3*x*. What one can see from Figure 10 is a weak tail starting from  $\sim 360 \text{ nm}$  and ending at  $\sim 450 \text{ nm}$  with  $\epsilon < 4000 \text{ mol}^{-1} \text{ L cm}^{-1}$ . This indicates that only has a portion of the diphenylacetylene pendants of P3*x* been polymerized into ODPA side chains with low degrees of polymerization (or small numbers of repeat units) and short conjugation lengths. The inhomogeneity in the conjugation lengths of the ODPA side chains as well as their random distributions along the PPA backbone of P3*x* have smoothened the defined absorption peak<sup>19</sup> into a gradually decaying tail.

As discussed in the Introduction, PPA and PDPA can efficiently emit blue and green lights, respectively, upon photoexcitation.<sup>12,13</sup> PPO is a typical example of PPA,<sup>5</sup> which emits a blue light of 460 nm in a high quantum efficiency ( $\Phi_{\rm F}$  43%).<sup>12,13</sup> Both P1 and P2 can be considered to be derivatives of PPO. Because of this structural similarity, P1 and P2 emit blue light of 460 nm with spectral profiles similar to that of PPO (Figure 11A). The quantum yield of P1 is the same as that of PPO, while P2 is a more efficient emitter with a higher quantum yield (59%).

Different from PPO, P3x emits a blue-green light of 491 nm, instead of a blue light of 460 nm. The energy



**Figure 10.** UV absorption spectra of THF solutions of P1 (sample taken from Table 1, no. 2), P2 (Table 1, no. 8), and P3x (Table 1, no. 10). The spectral data for poly(1-phenyl-1-octyne) (PPO)<sup>5</sup> and poly(1-{p-[(1-naphthyloxy)octyloxy]}phenyl-2-phenylacetylene) (PNOPPA)<sup>20</sup> are shown for comparison.

absorbed by the PPA backbone of P3x is transferred to its ODPA side chains, which pumps the oligomers to their excited states. When the excitons decay back to their ground state, a blue-green light is emitted from the ODPA chains. There is no shoulder at 460 nm in the photoluminescence spectrum of P3x, indicating that the energy transfer from the PPA backbone to the ODPA side chains is efficient. The emission spectrum of a PDPA chain is normally peaked at >500 nm:<sup>5,12,13</sup> for example, the  $\lambda_{max}$  of the spectrum of PNOPPA is located at ~509 nm (Figure 11B).<sup>20</sup> The blue shift of the  $\lambda_{max}$  of P3x from that of a normal PDPA chain confirms the finding by the UV spectral analysis: the effective conjugation length of the ODPA side chains of P3x is short.

While monomer **3** emits a deep-blue light of ~396 nm upon excitation at 368 nm, its polymer P**3**x emits faintly at ~396 nm when excited at 368 nm, as can be seen from the weak bump in the emission spectrum of P**3**x(Figure 9B). Its spectrum is dominated by the emission from its ODPA side chains at 491 nm. As the emission spectrum of the unpolymerized diphenylacetylene pendants of P**3**x overlaps with the absorption spectrum of its ODPA side chains (cf., Figures 10 and 11), the light emitted from its chromophoric pendants is reabsorbed by its ODPA side chains, hence the blue-green emission at 491 nm. The quantum yield for the emission of P**3**xgenerated by the excitation at 368 nm is 34%, which is



**Figure 11.** Photoluminescence spectra of THF solutions (0.05 mM) of (A) P1 (sample from Table 1, no. 2), P2 (Table 1, no. 8), P3x (Table 1, no. 10), and poly(1-phenyl-1-octyne) (PPO)<sup>5</sup> and (B) monomer **3**, its polymer P3x, and poly(1-{*p*-[(1-naphthyloxy)octyloxy]}phenyl-2-phenylacetylene) (PNOPPA)<sup>20</sup> recorded at excitation wavelengths of (A) 355 and (B) 368 nm.

lower than that for its emission generated by the excitation at 355 nm (57%). This is probably due to the less efficient energy transfer from the pendants to the ODPA chains, as evidenced by bump for the pendant emission at ~400 nm. With respect to the excitation wavelength, the quantum yields for OPDA emissions (43% and 57%) are always lower than that of PNOPPA (98%),<sup>20</sup> once again revealing the short effective conjugation length of the OPDA side chains.

### **Concluding Remarks**

In this work, a group of 1-phenyl-1-undecyne derivatives with different functional substituents (1-3) are successfully polymerized into high molecular weight polymers (P1-P3x) in satisfactory isolation yields. Spectroscopic characterizations reveal that P1 and P2 are linear chains while P3x possesses a nonlinear structure. The polyacetylenes are all solution-processable. The excellent solubility of P3x in common solvents is a nice surprise, because it is a cross-linked polymer.<sup>21</sup> All the polymers are stable. No change in  $M_w$  is observed when the polymers have been exposed to air for >4 years, although they contain double and/or triple bonds in their molecular structures. Little weight losses are detected when the polymers are heated to high temperatures ( $T_d \ge 390$  °C).

The disubstituted polyacetylenes with different pendant groups or side chains show different liquid-crystalline and light-emitting properties. The linear polymers with phenylcyclohexane- (P1) and phenyl benzoate-cored mesogenic pendants (P2) exhibit nematic and smectic mesomorphisms, respectively. In sharp contrast, the nonlinear polymer with diphenylacetylene-cored mesogenic pendants and ODPA side chains (P3x) is not liquid crystalline at all. All the polyacetylenes are efficient light emitters with  $\Phi_F$  in the range of 43–59% when excited at 355 nm. While P1 and P2 emit a blue light from their PPA backbones, P3x emits a blue-green light from its ODPA side chains due to the energy transfer from its backbone to the side chains.

Of particular interest is the successful synthesis of the soluble, cross-linked polyacetylene (P3x) under the normal acetylene polymerization conditions from the diyne monomer (3) with the two triple bonds in different chemical environments and with different reactivity or polymerizability. We have extended the utility of this synthetic strategy to the designs and preparations of soluble, cross-linked disubstituted polyenes with different molecular structures and varying light-emitting characteristics, full details of which will be reported in our future publications in due course.

## **Experimental Section**

**General Information.** Toluene (BDH) was predried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. Dichloromethane (Lab-Scan) was dried over molecular sieves and distilled over calcium hydride. Molybdenum(V) chloride was purchased from Acros and used as received. 4-(4-Pentylcyclohexyl)benzoic acid (5) and 4-(4-hexyloxyphenylcarbonyl-oxy)benzoic acid (6) were purchased from Slichem LCD Material Co., Ltd. All other reagents and solvents were purchased from Aldrich and used without further purification. 11-Phenyl-10-undecyn-1-ol (4) was prepared by coupling of 10-undecyn-1-ol with iodobenzene in the presence of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and Cul.<sup>33</sup> 4-Ethynylbenzoic acid (7) was synthesized according to our published procedures.<sup>34,35</sup>

The IR spectra were measured on a Perkin-Elmer 16 PC FT-IR spectrophotometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer using chloroform-*d* as the solvent and tetramethylsilane ( $\delta = 0$ ) or chloroform (7.26) as the internal reference. The UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. The fluorescence spectra were taken in THF on a SLM 8000C spectrofluorometer. The mass spectra were recorded on a Finnigan TSQ 7000 triple quadrupole mass spectrometer operating in a chemical ionization (CI) mode using methane as the carrier gas. The average molecular weights of the polymers were estimated by a Waters Associates GPC system. Degassed THF was used as the eluent at a flow rate of 1.0 mL/min. A set of monodisperse polystyrene standards covering the molecular weight range 10<sup>3</sup>-10<sup>7</sup> was used for the purpose of molecular weight calibration.

The thermal stability of the polymers was evaluated on a Perkin-Elmer TGA 7 under dry nitrogen at a heating rate of 20 °C/min. A Perkin-Elmer DSC 7 calorimeter was used to measure the mesophase transition thermograms at a scanning rate of 10 °C/min. An Olympus BX 60 POM equipped with a Linkam TMS 92 hot stage was used to observe the anisotropic optical textures. The XRD patterns were recorded on a Philips PW1830 powder diffractometer with a graphite monochromator using 1.5406 Å Cu K $\alpha$  wavelength at room temperature (scanning rate 0.05°/s, scan range 2–30°). The polymer samples for the XRD measurements were prepared by freezing the molecular arrangements in the liquid crystalline states by liquid nitrogen as previously reported.<sup>5,24,25</sup>

**Monomer Preparations.** 1-Phenyl-1-alkyne derivatives 1 and 2 were prepared by esterifications of 11-phenyl-10undecyn-1-ol (4) with 4-(4-pentylcyclohexyl)benzoic acid (5) and 4-(4-hexyloxyphenyl-carbonyloxy)benzoic acid (6), respectively, using DCC as a dehydrating agent (cf., Scheme 1). Diyne monomer 3 was synthesized by a multistep reaction route: esterification of 4-ethynylbenzoic acid (7) with 11-phenyl-10undecyn-ol (4) in the presence of DCC, TsOH, and DMAP, followed by coupling of the resultant intermediate 11-phenyl-10-undecynyl 4-ethynylbenzoate (8) with 4-heptyloxyiodobenzene (9) using  $PdCl_2(PPh_3)_2$  as the catalyst. A typical example of experimental procedures for the synthesis of 3 is given below.

11-Phenyl-10-undecynyl 4-Ethynylbenzoate (8). 11-Phenyl-10-undecyn-1-ol (4; 4.0 g, 16.3 mmol), 4-ethynylbenzoic acid (7; 2.9 g, 19.6 mmol), TsOH (0.6 g, 3.3 mmol), and DMAP (0.4 g, 3.3 mmol) were dissolved in 200 mL of dry dichloromethane in a 500 mL two-necked flask under nitrogen. The solution was cooled to 0-5 °C with an ice bath, to which 5.0 g of DCC (24.5 mmol) in 50 mL of dichloromethane was added under stirring via a dropping funnel with a pressure-equalization arm. The mixture was stirred at room-temperature overnight. After the formed insoluble crystals of urea were filtered out, the filtrate was concentrated by a rotary evaporator. The crude product was purified by a silica gel column using chloroform as the eluent. A pale yellow liquid was obtained in 78.6% yield.

11-[4-(4-Heptyloxyphenylethynyl)phenylcarbonyloxy]-1-phenyl-1-undecyne (3). Into a 500 mL two-necked flask were added 0.1 g (0.14 mmol) of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 0.1 mg  $(5 \times 10^{-4} \text{ mmol})$  of CuI, and 150 mL of a triethylamine solution of 9 (2.1 g, 10.5 mmol) under nitrogen. After all the catalysts were dissolved, 3.2 g of 8 (8.7 mmol) in 50 mL of triethylamine was injected into the flask. The mixture was stirred at 60 °C for 24 h. After the formed salt was filtered out, the solution was concentrated by a rotary evaporator. The product was purified by a silica gel column using chloroform/hexane (3:2 by volume) as the eluent. Recrystallization in ethanol/ water mixture (3:1 by volume) gave 3.0 g of product 3 as a white solid in 61.5% yield. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 2217 (C=C stretching). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.00 (d, 2H, Ar-H ortho to CO<sub>2</sub>), 7.56 (d, 2H, Ar-H meta to CO<sub>2</sub>), 7.48 (d, 2H, Ar-H meta to  $OC_7H_{15}$ ), 7.39 (m, 2H, Ar-H ortho to  $C = CCH_2$ ), 7.25 (m, 3H, Ar-H para and meta to  $C = CCH_2$ ), 6.98 (d, 2H, Ar-H ortho to OC<sub>7</sub>H<sub>15</sub>), 4.30 (t, 2H, ArCO<sub>2</sub>CH<sub>2</sub>), 3.97 (t, 2H, OCH<sub>2</sub>), 2.40 (m, 2H, =C-CH<sub>2</sub>), 1.74 (m, 4H, ArCO<sub>2</sub>- $CH_2CH_2$  and  $\equiv CCH_2CH_2$ ), 1.62 (m, 2H,  $OCH_2CH_2$ ), 1.45–1.31 [m, 18H, (CH<sub>2</sub>)<sub>9</sub>], 0.90 (t, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 166.0 (ArCO<sub>2</sub>), 159.2 (aromatic carbon linked to OC<sub>7</sub>H<sub>15</sub>), 133.1 (aromatic carbons meta to OC<sub>7</sub>H<sub>15</sub>), 131.5 (aromatic carbons ortho to C=C), 131.1 (aromatic carbons ortho to  $CO_2$ ), 129.4 (aromatic carbons meta and para to  $CO_2$ ), 128.2 (aromatic carbon linked to CO<sub>2</sub>), 128.1 (aromatic carbons meta to C=C), 127.4 (aromatic carbons para to C=C), 124.0 (aromatic carbon linked to C=C), 114.5 (aromatic carbon para to  $OC_7H_{15}$ ), 114.4 (aromatic carbons ortho to  $OC_7H_{15}$ ), 92.6  $(OCOArC \equiv), 90.3 (\equiv CCH_2), 87.4 (\equiv CArOC_7H_{15}), 80.6 (ArC \equiv)$ CCH<sub>2</sub>), 68.0 (OCH<sub>2</sub>), 65.1 (ArCO<sub>2</sub>CH<sub>2</sub>), 31.7, 29.3, 29.2, 29.1, 29.0, 28.8, 28.7, 28.6, 25.94, 25.90, 22.5, 19.3 ( $\equiv$ C-CH<sub>2</sub>), 14.0. MS(CI): m/e 563.4 [ $(M + 1)^+$ , calcd 563.4].

11-[4-(4-Pentylcyclohexyl)phenylcarbonyloxy]-1-phenyl-1-undecyne (1). It was prepared by the esterification of 4 with 5 using DCC as the dehydrating agent. A colorless liquid was obtained in 89.8% yield. (The absorption band of the 1-phenyl-1-alkyne triple bond in 1 was too weak to be identified in the IR spectrum.) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.96 (d, 2H, Ar-H ortho to CO<sub>2</sub>), 7.39 (m, 2H, Ar-H ortho to C≡C), 7.25 (m, 5H, Ar−H para and meta to C≡C and meta to CO<sub>2</sub>), 4.28 (t, 2H,  $ArCO_2CH_2$ ), 2.38 (m, 3H,  $\equiv C-CH_2$  and  $C-H_2$ para to C<sub>5</sub>H<sub>11</sub>), 1.85 (d, C-H meta to C<sub>5</sub>H<sub>11</sub>), 1.73 (m, 2H,  $ArCO_2CH_2CH_2$ ), 1.59 (m, 2H,  $\equiv CCH_2CH_2$ ), 1.48–1.22 [m, 17H, C-H linked to C<sub>5</sub>H<sub>11</sub> and (CH<sub>2</sub>)<sub>8</sub>], 0.90 [m, 5H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> and CH<sub>3</sub>)]  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 166.5 (ArCO<sub>2</sub>), 153.0 (aromatic carbon para to CO<sub>2</sub>), 131.4 (aromatic carbons ortho to C=C), 129.5 (aromatic carbons ortho to  $CO_2$ ), 128.0 (aromatic carbons para to CO<sub>2</sub>), 127.2 (aromatic carbons meta and para to C=C), 126.7 (aromatic carbons meta to CO<sub>2</sub>), 124.0 (aromatic carbon linked to C=C), 90.2 (ArC=), 80.5 (=CCH<sub>2</sub>), 64.7 (ArCO<sub>2</sub>CH<sub>2</sub>), 44.6, 37.2, 37.1, 33.9, 33.3, 32.1, 29.3, 29.1, 29.0, 28.8, 28.7, 26.5, 25.9, 22.6, 19.3, 14.0. MS(CI): m/e 501.4  $[(M + 1)^+, \text{ calcd } 501.4].$ 

11-[4-(4-Hexyloxyphenylcarbonyloxy)phenylcarbonyloxy]-1-phenyl-1-undecyne (2). White solid; yield: 55.7%. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 2231 (C=C stretching). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.12 (m, 4H, Ar-H ortho to CO<sub>2</sub>CH<sub>2</sub> and meta to OC<sub>6</sub>H<sub>13</sub>), 7.39 (m, 2H, Ar-H ortho to C≡C), 7.27 (m, 5H, Ar−H para and meta to C≡C and meta to CO<sub>2</sub>CH<sub>2</sub>), 6.97 (d, Ar-H ortho to OC<sub>6</sub>H<sub>13</sub>), 4.31 (t, 2H, ArCO<sub>2</sub>CH<sub>2</sub>), 4.03 (t, 2H, OCH<sub>2</sub>), 2.40 (t, 2H, ≡C−CH<sub>2</sub>), 1.80 (m, 4H,  $ArCO_2CH_2CH_2$  and  $\equiv C-CH_2CH_2$ ), 1.47 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 1.38–1.32 [m, 16H, (CH<sub>2</sub>)<sub>8</sub>], 0.93 (t, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>), δ (ppm): 165.6 (CH<sub>2</sub>OCO), 164.0 (ArOCO), 163.5 (aromatic carbon linked to OC<sub>6</sub>H<sub>13</sub>), 154.5 (aromatic carbon para to CO<sub>2</sub>CH<sub>2</sub>), 132.1 (aromatic carbons meta to  $OC_6H_{13}$ ), 131.3 (aromatic carbons ortho to C=C), 130.8 (aromatic carbons or the to  $CO_2CH_2$ ), 127.9 (aromatic carbon linked to  $CO_2CH_2$ ), 127.7 (aromatic carbons meta to C=C), 127.2 (aromatic carbons para to C=C), 123.9 (aromatic carbon linked to C=C), 121.6 (aromatic carbons meta to  $CO_2CH_2$ ), 120.8 (aromatic carbon para to OC<sub>6</sub>H<sub>13</sub>), 114.1 (aromatic carbons ortho to  $OC_6H_{13}$ ), 90.2 (ArC=), 80.4 (=CCH<sub>2</sub>), 68.0 (OCH<sub>2</sub>), 64.9 (ArCO<sub>2</sub>CH<sub>2</sub>), 31.3, 29.2, 29.0, 28.9, 28.8, 28.7, 28.54, 28.51, 25.8, 25.4, 22.4, 19.2, 13.9. MS(CI): m/e 569.4  $[(M + 1)^+, \text{ calcd 569.4}].$ 

**Polymer Syntheses.** All of the polymerization reactions and manipulations were carried out under nitrogen using Schlenk techniques in a vacuum line system or an inertatmosphere glovebox (Vacuum Atmospheres), except for the purification of the polymers, which was done in an open atmosphere. A typical experimental procedure for the polymerization of **3** or for the synthesis of P3x is given below:

Into a baked 20 mL Schlenk tube with a stopcock in the sidearm was added 440.5 mg (0.78 mmol) of 3. The tube was evacuated under vacuum and then flushed with nitrogen three times through the sidearm. Freshly distilled toluene (2 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 15.9 mg of tungsten(VI) chloride and 17.2 mg of tetraphenyltin in 2 mL of toluene. The two tubes were aged at 60 °C for 15 min and then the monomer solution was transferred to the catalyst solution using a hypodermic syringe. The reaction mixture was stirred at room temperature under nitrogen for 24 h. The solution was then cooled to room temperature, diluted with 5 mL of chloroform, and added dropwise to 500 mL of acetone through a cotton filter under stirring. The precipitate was allowed to stand overnight and then filtered with a Gooch crucible. The polymer was washed with acetone and dried in a vacuum oven to a constant weight.

**Characterization Data. P1.** Yellow powder: yield 68.5%.  $M_{\rm w}$  62400;  $M_{\rm w}/M_{\rm n}$  2.3 (GPC; Table 1, no. 2). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.94 (Ar–H ortho to CO<sub>2</sub>), 7.23 (Ar–H meta to CO<sub>2</sub>), 4.26 (ArCO<sub>2</sub>CH<sub>2</sub>), 2.50 (C–H para to C<sub>5</sub>H<sub>11</sub>), 1.87 (C–H meta to C<sub>5</sub>H<sub>11</sub>), 1.72 (ArCO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> and =CCH<sub>2</sub>CH<sub>2</sub>), 1.32 [(CH<sub>2</sub>)<sub>8</sub>], 0.93 [CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>], 0.91 (CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 166.3 (ArCO<sub>2</sub>), 152.8 (aromatic carbon para to CO<sub>2</sub>), 129.4 (aromatic carbons ortho to CO<sub>2</sub>), 127.9 (aromatic carbons para to CO<sub>2</sub>), 126.6 (aromatic carbons meta to CO<sub>2</sub>), 64.8 (ArCO<sub>2</sub>CH<sub>2</sub>), 44.8, 37.4, 37.3, 34.1, 33.5, 32.3, 29.5, 28.9, 26.8, 26.2, 22.8, 14.3. UV (THF, 8.0 × 10<sup>-5</sup> mol/L),  $\lambda_{\rm max}$  (nm)/ $\epsilon_{\rm max}$  (mol<sup>-1</sup> L cm<sup>-1</sup>): 240/1.86 × 10<sup>4</sup>, 332/2.55 × 10<sup>3</sup>. PL (THF, 5.0 × 10<sup>-5</sup> mol/L),  $\lambda_{\rm max}$ : 460 nm;  $\Phi_{\rm F}$ : 43%.

**P2.** Yellow powder: yield 86.2%.  $M_w$  36100;  $M_w/M_n$  1.6 (GPC; Table 1, no. 9). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.06 (Ar–H ortho to CO<sub>2</sub>CH<sub>2</sub> and meta to OC<sub>6</sub>H<sub>13</sub>), 7.22 (Ar–H meta to CO<sub>2</sub>CH<sub>2</sub>), 6.92 (Ar–H ortho to OC<sub>6</sub>H<sub>13</sub>), 4.26 (ArCO<sub>2</sub>CH<sub>2</sub>), 3.99 (OCH<sub>2</sub>), 1.79 (ArCO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> and =C–CH<sub>2</sub>CH<sub>2</sub>), 1.45 (OCH<sub>2</sub>CH<sub>2</sub>), 1.34 [(CH<sub>2</sub>)<sub>8</sub>], 0.90 (t, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 165.7 (CH<sub>2</sub>OCO), 164.2 (ArOCO), 163.6 (aromatic carbon linked to OC<sub>6</sub>H<sub>13</sub>), 154.6 (aromatic carbon para to CO<sub>2</sub>CH<sub>2</sub>), 127.8 (aromatic carbon linked to CO<sub>2</sub>CH<sub>2</sub>), 127.7 (aromatic carbons meta to CO<sub>2</sub>CH<sub>2</sub>), 121.0 (aromatic carbon para to OC<sub>6</sub>H<sub>13</sub>), 68.2 (OCH<sub>13</sub>), 114.1 (aromatic carbons ortho to OC<sub>6</sub>H<sub>13</sub>), 68.2

(ArCO<sub>2</sub>CH<sub>2</sub>), 31.4, 28.9, 28.7, 25.9, 25.5, 22.5, 13.9. UV (THF, 7.0 × 10<sup>-5</sup> mol/L),  $\lambda_{max}$  (nm)/ $\epsilon_{max}$  (mol<sup>-1</sup> L cm<sup>-1</sup>): 264/2.22 × 10<sup>4</sup>, 330/2.10 × 10<sup>3</sup>. PL (THF, 5.0 × 10<sup>-5</sup> mol/L),  $\lambda_{max}$ : 460 nm;  $\Phi_{\rm F}$ : 59%.

**P3x.** Yellow-green powder: yield 32.4%.  $M_{\rm w}$  50500;  $M_{\rm w}/M_{\rm p}$ 1.7 [GPC (for the main GPC peak in the "normal" molecular weight region); Table 1, no. 10). IR (KBr),  $\nu$  (cm<sup>-1</sup>): 2214 (C=C stretching). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.96  $(Ar-H \text{ ortho to } CO_2)$ , 7.50  $(Ar-H \text{ meta to } CO_2 \text{ and } OC_7H_{15})$ , 6.84 (Ar-H ortho to  $OC_7H_{15}$ ), 4.26 (ArCO<sub>2</sub>CH<sub>2</sub>), 3.94 (OCH<sub>2</sub>), 2.34 (=C-CH<sub>2</sub>), 1.78 (ArCO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> and =CCH<sub>2</sub>CH<sub>2</sub>), 1.32 [OCH<sub>2</sub>CH<sub>2</sub> and (CH<sub>2</sub>)<sub>9</sub>], 0.89 (CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 165.9 (ArCO<sub>2</sub>), 159.4 (aromatic carbon linked to OC7H15), 133.1 (aromatic carbons meta to OC7H15), 31.1 (aromatic carbons ortho to CO<sub>2</sub>), 129.3 (aromatic carbons meta and para to  $CO_2$ ), 128.1 (aromatic carbon linked to  $CO_2$ ), 114.5 (aromatic carbons para and meta to  $OC_7H_{15}$ ), 92.5 (OCOArC= ), 87.5 ( $\equiv CArOC_7H_{15}$ ), 68.1 (OCH<sub>2</sub>), 65.2 (ArCO<sub>2</sub>CH<sub>2</sub>), 31.8, 29.2, 29.1, 28.8, 26.0, 22.7, 14.0. UV (THF,  $8.5 \times 10^{-5}$  mol/L),  $\lambda_{\rm max}$  (nm)/ $\epsilon_{\rm max}$  (mol<sup>-1</sup> L cm<sup>-1</sup>): 316/2.51  $\times$  10<sup>4</sup>. PL (THF,  $5.0 \times 10^{-5}$  mol/L),  $\lambda_{max}$ : 491 nm;  $\Phi_F$ : 57%.

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#### **References and Notes**

- Nobel lectures: (a) Shirakawa, H. Angew. Chem., Int. Ed. 2001, 40, 2575–2580. (b) MacDiarmid, A. G. Angew. Chem., Int. Ed. 2001, 40, 2581–2590. (c) Heeger, A. J. Angew. Chem., Int. Ed. 2001, 40, 2591–2611.
- (2) (a) Chien, J. C. W. Polyacetylene: Chemistry, Physics, and Material Science; Academic Press: New York, 1984.
  (b) Conjugated Oligomers, Polymers, and Dendrimers; Brédas, J. L., Ed.; De Boeck Université: Paris, France, 1999.
- (3) For reviews, see: (a) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.-Eur. J.* **2004**, *10*, 43-51. (b) Sedlacek, J.; Vohlidal, J. Collect. Czech. Chem. Commun. **2003**, 68, 1745-1790. (c) Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau, Z. Prog. Polym. Sci. **2001**, *26*, 721-798. (d) Choi, S. K.; Gal, Y. S.; Jin, S. H.; Kim, H. K. Chem. Rev. **2000**, *100*, 1645-1681. (e) Ginsburg, E. J.; Gorman, C. B.; Grubbs, R. H. In Modern Acetylene Chemistry; Stang, P. J.; Diederich, F., Eds.; VCH: Weinheim, Germany, 1995; Chapter 10. (f) Saunders, R. S.; Cohen, R. E.; Schrock, R. R. Acta Polym. **1994**, *45*, 301-307.
- (4) For reviews, see: (a) Cheuk, K. K. L.; Li, B. S.; Tang, B. Z. In Encyclopedia of Nanoscience and Nanotechnology; Nalwa, H. S., Ed.; American Scientific Publishers: Stevenson Ranch, CA, 2004; Vol. 8, pp 703-713. (b) Lam, J. W. Y.; Chen, J.; Law, C. C. W.; Peng, H.; Xie, Z.; Cheuk, K. K. L.; Kwok, H. S.; Tang, B. Z. Macromol. Symp. 2003, 196, 289-300. (c) Xie, Z.; Peng, H.; Lam, J. W. Y.; Chen, J.; Zheng, Y.; Qiu, C.; Kwok, H. S.; Tang, B. Z. Macromol. Symp. 2003, 195, 179-184. (d) Cheuk, K. K. L.; Li, B. S.; Tang, B. Z. Curr. Trends Polym. Sci. 2002, 7, 41-55. (e) Tang, B. Z. Polym. News 2001, 26, 262-272.
- (5) For a review, see: Lam, J. W. Y.; Tang, B. Z. J. Polym. Sci., Part A: Polym. Chem. 2003, 41, 2607–2629.
- (6) (a) Masuda, T.; Tang, B. Z.; Higashimura, T.; Yamaoka, H. Macromolecules 1985, 18, 2369–2373. (b) Masuda, T.; Tang, B. Z.; Tanaka, T.; Higashimura, T. Macromolecules 1986, 19, 1459–1464.
- (7) For reviews, see: (a) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. Nature (London) 1999, 397, 121–128.
  (b) Soos, Z. G.; Galvao, D. S.; Etemad, S. Adv. Mater. 1994, 6, 280–287.

- (8) (a) Sanda, F.; Nakai, T.; Kobayashi, N.; Masuda, T. Macromolecules 2004, 37, 2703-2708. (b) Yu, G.; Liu, Y. Q.; Zhan, X. W.; Li, H. Y.; Yang, M. J.; Zhu, D. B. Thin Solid Films 2000, 363, 126-129. (c) Wang, Y. Z.; Sun, R. G.; Wang, D. K.; Swager, T. M.; Epstein, A. J. Appl. Phys. Lett. 1999, 74, 2593-2595. (d) Hidayat, R.; Hirohata, M.; Fujii, A.; Teraguchi, M.; Masuda, T.; Yoshino, K. Jpn. J. Appl. Phys. 1999, 38, 931-935.
- (9) (a) Chen, J.; Xie, Z. Lam, J. W. Y.; Law, C. C. W.; Tang, B. Z. Macromolecules 2003, 36, 1108–1117. (b) Lam, J. W. Y.; Law, C. K.; Dong, Y.; Wang, J.; Ge, W.; Tang, B. Z. Opt. Mater. 2002, 21, 321–324. (c) Lam, J. W. Y.; Dong, Y.; Luo, J. Cheuk, K. K. L.; Xie, Z.; Tang, B. Z. Thin Solid Films 2002, 417, 143–146. (d) Lam, J. W. Y.; Dong, Y.; Cheuk, K. K. L.; Luo, J.; Xie, Z.; Kwok, H. S.; Mo, Z.; Tang, B. Z. Macromolecules 2002, 35, 1229–1240. (e) Lee, P. P. S.; Geng, Y.; Kwok, H. S.; Tang, B. Z. Thin Solid Films 2000, 363, 149–151. (f) Huang, Y. M.; Lam, J. W. Y.; Cheuk, K. K. L.; Ge, W.; Tang, B. Z. Macromolecules 1999, 32, 5976–5978. (g) Huang, Y. M.; Ge, W.; Lam, J. W. Y.; Tang, B. Z. Appl. Phys. Lett. 1999, 75, 4094–4096.
- (10) (a) Ting, C. H.; Hsu, C. S. Jpn. J. Appl. Phys. 2001, 40, 5342–5345. (b) Sun, R. G.; Wang, Y. Z.; Wang, D. K.; Zheng, Q. B.; Epstein, A. J. Synth. Met. 2000, 111, 403–408. (c) Hidayat, R.; Tatsuhara, S.; Kim, D. W.; Ozaki, M.; Yoshino, K.; Teraguchi, M.; Masuda, T. Phys. Rev. B 2000, 61, 10167–10173. (d) Frolov, S. V.; Fujii, A.; Chinn, D.; Hirohata, M.; Hidayat, R.; Taraguchi, M.; Masuda, T.; Yoshino, K.; Vardeny, Z. V. Adv, Mater. 1998, 10, 869–872. (e) Sun, R. G.; Masuda, T.; Kobayashi, T. Synth. Met. 1997, 91, 301–303.
- (11) (a) Xie, Z.; Lam, J. W. Y.; Dong, Y.; Qiu, C.; Kwok, H. S.; Tang, B. Z. Opt. Mater. 2002, 21, 231–234. (b) Tang, B. Z. Xu, H.; Lam, J. W. Y.; Lee, P. P. S.; Xu, K.; Sun, Q.; Cheuk, K. K. L. Chem. Mater. 2000, 12, 1446–1455.
- (12) (a) Sun, R. G.; Zheng, Q. B.; Zhang, X. M.; Masuda, T.; Kobayashi, T. Jpn. J. Appl. Phys. **1999**, 38, 2017–2023. (b) Tada, K.; Hidayat, R.; Hirohata, M.; Teraguchi, M.; Masuda, T.; Yoshino, K. Jpn. J. Appl. Phys. **1996**, 35, 1138–1141.
- (13) Fujii, A.; Hidayat. R.; Sonoda, T.; Fujisawa, T.; Ozaki, M.; Vardeny, Z. V.; Teraguchi, M.; Masuda, T.; Yoshino, K. Synth. Met. 2001, 116, 95-99.
- (14) (a) Tang, B. Z.; Lam, J. W. Y.; Lai, L. M.; Xie, Z.; Kwok, H. S. *Proc. SPIE* 2003, *5213*, 15–25. (b) Tang, B. Z.; Lam, J. W. Y.; Luo, J.; Dong, Y.; Cheuk, K. K. L.; Xie, Z.; Kwok, H. S. *Proc. SPIE* 2001, *4463*, 132–138.
- (15) Dong, Y. P.; Lam, J. W. Y.; Peng, H.; Cheuk, K. K. L.; Kwok, H. S.; Tang, B. Z. *Macromolecules* **2004**, *37*, 6408–6417.
- (16) (a) McArdle, C. B. Side Chain Liquid Crystal Polymers; Blackie: London, 1989. (b) Handbook of Liquid Crystal Research, Collings, P. J., Patel, J. S., Eds.; Oxford University Press: New York, 1997.
- (17) (a) Kong, X.; Tang, B. Z. Chem. Mater. 1998, 10, 3352–3363.
  (b) Tang, B. Z.; Kong, X.; Wan, X.; Peng, H.; Lam, W. Y.; Feng, X.; Kwok, H. S. Macromolecules 1998, 31, 2419–2432.
- (18) Shirakawa, H.; Masuda, T.; Takeda, K. In The Chemistry of Triple-Bonded Functional Groups; Patai, S., Ed.; Wiley: New York, 1994. Supplement C2; Vol. 2; Chapter 17, pp 945–1016.
- (19) (a) Tsuchihara, K.; Masuda, T.; Higashimura, T. Macromolecules 1992, 25, 5816–5820. (b) Tachimori, H.; Masuda, T.; Kouzai, H.; Higashimura, T. Polym. Bull. (Berlin) 1994, 32, 133–140. (c) Kouzai, H.; Masuda, T.; Higashimura, T. Polymer 1994, 35, 4920–4923.
- (20) (a) Law, C. C. W.; Lam, J. W. Y.; Dong, Y. P.; Tang, B. Z. Polym. Prepr. 2004, 45 (2), 839-840. (b) Law, C. C. W. M.Philos. Thesis, The Hong Kong University of Science & Technology, Aug 2004.
- (21) (a) Li, F. X.; Lu, Z. F.; Qian, H. T.; Rui, J. M.; Chen, S. N.; Jiang, P.; An, Y. L.; Mi, H. F. Macromolecules 2004, 37, 764– 768. (b) Schmitz, K. S.; Wang, B.; Kokufuta, E. Macromolecules 2001, 34, 8370–8377. (c) Downey, J. S.; McIsaac, G.; Frank, R. S.; Stöver, H. D. H. Macromolecules 2001, 34, 4534–4541 (d) Lindenblatt, G.; Schartl, W.; Pakula, T.; Schmidt, M. Macromolecules 2000, 33, 9340–9347. (e) Okay, O.; Durmaz, S.; Erman, B. Macromolecules 2000, 33, 4822– 4827. (f) Szuromi, E.; Berka, M.; Borbely, J. Macromolecules 2000, 33, 3993–3998. (g) Fernández-Nieves, A.; Fernández-Barbero, A.; Vncent, B.; de las Nieves, F. J. Macromolecules 2000, 33, 2114–2118.
- (22) Silverstein, R. M.; Webster, F. X. Spectrometric Identification of Organic Compounds, 6th ed.; Wiley: New York, 1998.
- (23) Sun, Q.; Xu, K.; Peng, H.; Zheng, R.; Häussler, M.; Tang, B. Z. Macromolecules **2003**, *36*, 2309–2320.

- (24) (a) Lam, J. W. Y.; Dong, Y.; Cheuk, K. K. L.; Luo, J.; Xie, Z.; Kwok, H. S.; Mo, Z.; Tang, B. Z. *Macromolecules* **2002**, *35*, 1229–1240. (b) Lam, J. W. Y.; Kong, X.; Dong, Y.; Cheuk, K. K. L.; Xu, K.; Tang, B. Z. *Macromolecules* **2000**, *33*, 5027– 5040.
- (25) Kong, X.; Lam, J. W. Y.; Tang, B. Z. Macromolecules 1999, 32, 1722–1730.
- (26) Häussler, M.; Zheng, R.; Lam, J. W. Y.; Tong, H.; Dong, H.; Tang, B. Z. J. Phys. Chem. B 2004, 108, 10645–10650.
- (27) (a) Demus, D.; Richter, L. Textures of Liquid Crystals; Verlag Chemie: Weinheim, Germany, 1978. (b) Gray, G. W.; Goodby, J. W. G. Smectic Liquid Crystals: Texture and Structures; Leonard Hill: London, 1984.
- (28) (a) Goto, H.; Akagi, K.; Shirakawa, H.; Oh, S.-Y.; Araya, K. Synth. Met. 1995, 71, 1899–1900. (b) Akagi, K.; Goto, H.; Shirakawa, H.; Oh, S.-Y, Araya, K. Synth. Met. 1995, 69, 13– 16. (c) Oh, S.-Y.; Akagi, K.; Shirakawa, H.; Araya, K. Macromolecules 1993, 26, 6203–6206.
- (29) Lam, W. Y.; Kong, X.; Tang, B. Z. Polym. Mater. Sci. Eng. 1999, 80, 159–160.

- (30) Lam, J. W. Y. M.Philos. Thesis, The Hong Kong University of Science & Technology, Aug 1998.
- (31) (a) Liquid Crystalline Order in Polymers; Blumstein, A., Hsu, E. C., Eds.; Academic Press: New York, 1978. (b) Mariani, P.; Rustichelli, F.; Torquati, G. In Physics of Liquid Crystalline Materials; Khoo, I.-C., Simoni, F., Eds.; Gordon & Breach Science: New York, 1991; Chapter 1.
- (32) Masuda, T.; Takahashi, T.; Higashimura; T. Macromolecules 1985, 18, 311–317.
- (33) Lam, J. W. Y. Ph.D. Dissertation, The Hong Kong University of Science & Technology, Jan 2003.
- (34) Tang, B. Z.; Kong, X.; Wan, X.; Feng, X.-D. Macromolecules 1997, 30, 0, 5620–5628.
- (35) Cheuk, K. K. L.; Lam, J. W. Y.; Chen, J.; Lai, L. M.; Tang, B. Z. Macromolecules **2003**, *36*, 5947–5959.

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