Syntheses and Mesomorphic and Luminescent Properties of Disubstituted Polyacetylenes Bearing Biphenyl Pendants

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Received May 9, 2004; Revised Manuscript Received June 17, 2004

ABSTRACT: Liquid-crystalline and light-emitting poly(2-alkyne)s and poly(1-phenyl-1-alkyne)s containing biphenyl (Biph) cores, alkyl spacers, and alkoxy tails $(-\{RC=C[(CH_2)_m-OCO-Biph-OC_7H_{15}]\}_n$, where R, $m = CH_3$, 4 [P1(4)]; CH₃, 9 [P1(9)]; C₆H₅, 4 [P2(4)]; and C₆H₅, 9 [P2(9)], were synthesized and the effects of the spacer length and backbone structure on the properties of the polymers were investigated. The disubstituted acetylene monomers [1(m) and 2(m) (m = 4, 9) were prepared by esterification of biphenylcarboxylic acid (6) with ω -alkynyl alcohols [4(m) or 5(m)]. Polymerizations of 1(m) and 2(m) were effected by WCl_6- , $MoCl_5-$, and $NbCl_5-Ph_4Sn$ and the reactions catalyzed by WCl_6-Ph_4Sn under optimal conditions produce polymers P1(m) and P2(m) with high molecular weights (M_w up to 3.1×10^5) in good yields (up to 81%). The structures and properties of the disubstituted polyacetylenes were characterized and evaluated by nuclear magnetic resonance (NMR), thermogravimetry (TGA), differential scanning calorimetry (DSČ), polarized optical microscope (POM), X-ray diffraction (XRD), ultraviolet spectroscopy (UV), and photoluminescence (PL) analyses. The polymers are resistant to thermolysis ($T_d \ge 360$ °C) and all but P2(4) exhibit liquid crystallinity at elevated temperatures. The polymers with long methylene spacers, that is, P1(9) and P2(9), form a smectic A (SmA) mesophase with a monolayer arrangement. Upon excitation, strong UV and blue emissions peaking at 369 and 460 nm are observed in P1(m) and $P\hat{z}(m)$, respectively, whose quantum yields are found to increase with the spacer lengths.

Introduction

Conjugated polymers containing mesogenic and chromophoric units can potentially show very high carrier mobility and emit polarized light¹ and may find unique applications and stimulate technological innovations in the development of novel electronic and photonic devices such as light-emitting diodes, photovoltaic cells, thinfilm transistors, and plastic lasers.^{2,3} Realization of these captivating potentials requires the development of versatile processes for the syntheses of such polymers. Polyacetylene is an archetypal conjugated macromolecule and its functionalization has attracted much synthetic effort over the past decades.³⁻⁶ A variety of polyacetylenes containing liquid-crystalline mesogens⁷⁻⁹ and light-emitting chromophores⁹⁻¹¹ have been prepared, almost all of which are, however, monosubstituted from a structural viewpoint. These monosubstituted polyacetylenes show multifaceted mesophases, with their transition temperatures tunable by their molecular structures.^{5a,8,12} The mesogenic orientations of the polymers and their molecular arrangements can be readily manipulated by such external stimuli as mechanical forces¹³ and electrical field.¹⁴

Monosubstituted polyacetylenes have, however, been generally regarded as inefficient light emitters, with poly(phenylacetylene) and its derivatives being particularly weak fluorophores. We have previously developed a group of poly(1-alkyne) derivatives that fluoresce efficiently, whose emitting centers are, however, the chromophoric pendant groups rather than the conjugated polyene backbones.^{9,11} Certain disubstituted poly-

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acetylenes are known to emit strongly from their polyene backbones.^{15,16} Attachment of chromophoric and mesogenic pendants to disubstituted polyacetylene backbones may further enhance their emission efficiencies through pendant-to-backbone energy transfer as well as endowing them with liquid crystallinity. The creation of liquid-crystalline disubstituted polyacetylenes has been synthetically difficult. The only attempt, to our knowledge, is a one-page report in which the authors briefly described the polymerization of a mesogenic disubstituted acetylene catalyzed by TaCl₅–(n-C4H₉)₄-Sn, which gave an oligomer with an M_n of 4600 in a yield as low as 18%.¹⁷

We rose to the synthetic challenge and succeeded, in our previous work, in the synthesis of a group of disubstituted polypropiolates containing biphenyl-type mesogens and chromophores with high molecular weights (M_w up to 3.5×10^5) in good yields (up to $\sim 57\%$) (Chart 1).¹⁸ The polymers show mesomorphic smecticity and emit strong UV light ($\lambda_{max} = 369$ nm and $\Phi_F = 70\%$ when excited at 333 nm). The color of the emission indicates that the fluorescence is from the biphenyl

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pendant instead of the polypropiolate backbone. In other words, the polyene backbone with the ester group in its immediate vicinity is not luminescent. In this work, we designed a series of new disubstituted acetylenes without the ester groups in the close neighborhood of the triple bonds [1(m) and 2(m)] to check how this structural variation will affect the polymerization behavior of the monomers and the material properties of their polymers.¹⁹ The polymerizabilities of 1(m) and 2(m) were found to be quite different from those of the propiolates, but we eventually succeeded in converting them into high molecular weight polymers via optimization of reaction conditions. The polymer with a long alkyl spacer (m = 9) exhibits smecticity, irrespective of whether it is a poly(2-alkyne) [P1(9)] or poly(1-phenyl-1-alkyne) derivative [P2(9)]. The luminescence behaviors of polymers P1(m) and P2(m) are similar to and different from those of the polypropiolates,¹⁸ respectively: P1(m) emit UV light from their biphenyl pendants, while P2(*m*) emit blue light from their polyene backbones.

Results and Discussion

Monomer Syntheses. Four disubstituted acetylene monomers were prepared by esterification of 4'-heptyloxy-4-biphenylcarboxylic acid (**6**) with ω -alkynyl alcohols [**4**(*m*) or **5**(*m*)] in the presence of 1,3-dicyclohexylcarbodiimine (DCC), *p*-toluenesulfonic acid (TsOH), and 4-(dimethylamino)pyridine (DMAP; Scheme 1). All the reactions went smoothly and the monomers were isolated in high yields (72–88%). All the monomers were characterized by standard spectroscopic methods, from which satisfactory analysis data were obtained (see Experimental Section for details).

The disubstituted acetylene monomers are white solids at room temperature. None of them exhibits liquid crystallinity at elevated temperatures. In our search for liquid-crystalline acetylene monomers and polymers, we have found that most monosubstituted acetylene monomers containing the biphenylester groups are mesomorphic.^{8,9} The nonmesomorphism of the disubstituted acetylene monomers 1(m) and 2(m) suggests that the acetylenic proton plays an important role in the formation of mesophases in the monosubstituted acetylene monomers.

Polymerization Behaviors. Many nonmesomorphic calamitic monomers become liquid crystalline after polymerization due to the involved "polymer effect".²⁰ We tried to polymerize the disubstituted acetylene monomers 1(m) and 2(m) in the hope that the polym-

 Table 1. Polymerization of 7-{[(4'-Heptyloxy

 4-biphenylyl)carbonyl]oxy}-2-heptyne [1(4)]^a

no.	catalyst	solvent	temp (°C)	yield (%)	$M_{ m w}{}^b$	$M_{ m w}/M_{ m n}{}^b$
1	WCl ₆ -Ph ₄ Sn	dioxane	60	0		
2	WCl ₆ -Ph ₄ Sn	toluene	\mathbf{rt}^{c}	79.2	312 000	5.9
3	WCl ₆ -Ph ₄ Sn	toluene	60	81.4	254 000	7.0
4	MoCl ₅ -Ph ₄ Sn	toluene	60	22.4	872 000	12.4
5	NbCl ₅ -Ph ₄ Sn	toluene	60	0		
6	TaCl ₅ -Ph ₄ Sn	toluene	60	0		

^{*a*} Carried out under nitrogen for 24 h; $[M]_0 = 0.2$ M, [cat.] = [cocat.] = 10 mM. ^{*b*} Determined by GPC in THF on the basis of a polystyrene calibration. ^{*c*} Room temperature.

 Table 2. Polymerization of 12-{[(4'-Heptyloxy

 4-biphenylyl)carbonyl]oxy}-2-dodecyne [1(9)]^a

no.	catalyst	solvent	temp (°C)	yield (%)	$M_{ m w}{}^b$	$M_{\rm w}/M_{\rm n}{}^b$
1	WCl ₆ -Ph ₄ Sn	dioxane	60	trace		
2	WCl ₆ -Ph ₄ Sn	toluene	\mathbf{rt}^{c}	trace		
3	WCl ₆ -Ph ₄ Sn	toluene	60	80.7	22 600	8.9
4	WCl ₆ -Ph ₄ Sn	toluene	80	58.5	75 200	10.4
5	MoCl ₅ -Ph ₄ Sn	toluene	60	20.3	$157 \ 500^d$	15.9
6	NbCl ₅ -Ph ₄ Sn	toluene	60	28.3	4500 ^e	2.7
7	TaCl ₅ -Ph ₄ Sn	toluene	60	0		

^{*a*} Carried out under nitrogen for 24 h; $[M]_0 = 0.2$ M, [cat.] = [cocat.] = 10 mM. ^{*b*} Determined by GPC in THF on the basis of a polystyrene calibration. ^{*c*} Room temperature. ^{*d*} Soluble fraction. ^{*e*} Mixture of oligomer and trimer.

erization would help realize liquid crystallinity in the polymer systems. Tungsten and molybdenum chlorides are the most commonly used catalysts for acetylene polymerizations.^{9,21} These chlorides have, however, often been found to be incapable of initiating the polymerizations of acetylene monomers containing polar functional groups.²² Polymerizations of monomers 1(m) and 2(m) may thus be difficult because they contain the polar ester and ether units.

We first attempted to polymerize 1(4) using WCl₆- Ph_4Sn as catalyst. Stirring a dioxane solution of 1(4)under nitrogen in the presence of the W mixture at 60 °C for 24 h, however, gives no polymeric product (Table 1, no. 1). The reaction carried out in toluene with the same W mixture at room temperature, delightfully, produces a gray powdery solid in \sim 79% yield. Analysis by gel-permeation chromatography (GPC) gives an $M_{\rm w}$ of 3.1×10^5 and a polydispersity index (M_w/M_n) of 5.9, confirming the polymeric nature of the reaction product. Raising the temperature to 60 °C did not affect the reaction output much. MoCl₅-Ph₄Sn can also initiate the polymerization of 1(4), giving a polymer with a very high molecular weight (8.7×10^5) in a moderate yield (Table 1, no. 4). Generally speaking, the W mixture is a better catalyst than the Mo one in the polymerization of **1**(4), which is different from what we observed in the polymerization of its propiolate counterpart, where the Mo catalyst performed much better than the W one.¹⁸ This clearly demonstrates how variation in the molecular structure changes polymerization behavior of an acetylene monomer. Our attempts in using NbCl₅- and $TaCl_5-Ph_4Sn$ as catalysts for polymerization of 1(4)failed, possibly owing to the "toxic" interactions of the ester and ether functional groups with the transitionmetal mixtures or to the formation of oligomeric species that were soluble in the precipitating solvent.

Table 2 lists the polymerization results of 1(9). Like 1(4), 1(9) cannot be effectively polymerized by WCl₆– Ph₄Sn in dioxane. Surprisingly, the polymerization

Table 3. Polymerization of 6-{[(4'-Heptyloxy-4biphenylyl)carbonyl]oxy}-1-phenyl-1-hexyne [2(4)]^a

no.	catalyst	solvent	temp (°C)	yield (%)	$M_{ m w}{}^b$	$M_{ m w}/M_{ m n}{}^b$
1	WCl ₆ -Ph ₄ Sn	dioxane	60	trace		
2	WCl ₆ -Ph ₄ Sn	toluene	\mathbf{rt}^{c}	trace		
3	WCl ₆ -Ph ₄ Sn	toluene	60	63.2	63 000	1.9
4	WCl ₆ -Ph ₄ Sn	toluene	80	78.0	62 000	1.9
5	MoCl ₅ -Ph ₄ Sn	toluene	60	0		
6	NbCl ₅ -Ph ₄ Sn	toluene	60	0		
7	TaCl ₅ -Ph ₄ Sn	toluene	60	0		

^{*a*} Carried out under nitrogen for 24 h; $[M]_0 = 0.2$ M, [cat.] = [cocat.] = 10 mM. ^{*b*} Determined by GPC in THF on the basis of a polystyrene calibration. ^{*c*} Room temperature.

Table 4. Polymerization of 11-{[(4'-Heptyloxy-4biphenylyl)carbonyl]oxy}-1-phenyl-1-undecyne [2(9)]^a

no.	catalyst	solvent	temp (°C)	yield (%)	$M_{ m w}{}^b$	$M_{ m w}/M_{ m n}{}^b$
1	WCl ₆ -Ph ₄ Sn	dioxane	60	trace		
2	WCl ₆ -Ph ₄ Sn	toluene	\mathbf{rt}^{c}	45.1	13 100	2.0
3	WCl ₆ -Ph ₄ Sn	toluene	60	48.7	43 900	2.1
4	WCl ₆ -Ph ₄ Sn	toluene	80	66.4	53 400	1.8
5	MoCl ₅ -Ph ₄ Sn	toluene	60	0		
6	NbCl ₅ -Ph ₄ Sn	toluene	60	trace		
7	$TaCl_5-Ph_4Sn$	toluene	60	0		

^{*a*} Carried out under nitrogen for 24 h; $[M]_0 = 0.2$ M, [cat.] = [cocat.] = 10 mM. ^{*b*} Determined by GPC in THF on the basis of a polystyrene calibration. ^{*c*} Room temperature.

catalyzed by the same catalyst in toluene at room temperature yields almost no polymer (Table 2, no. 2), which is in sharp contrast to the fact that the polymerization of 1(4) under similar conditions gives a high molecular weight polymer in a high yield (cf., Table 1, no. 2). Fortunately, the polymerization of 1(9) proceeds well at 60 °C and produces a polymer in a high yield. Further raising the temperature to 80 °C decreases the yield but increases the M_w by more than 3-fold. MoCl₅– Ph₄Sn can polymerize 1(9) but the resultant polymer is only partially soluble. NbCl₅–Ph₄Sn can oligomerize 1(9) but its Ta counterpart is totally ineffective.

While WCl_6 -Ph₄Sn is ineffective in polymerizing **2**(4) in dioxane, it can initiate the polymerization of this monomer in toluene at elevated temperatures, yielding polymers with high molecular weights (Table 3). The attempted polymerizations of 2(4) by MoCl₅-, NbCl₅-, and TaCl₅-Ph₄Sn all end up in dismay. The effects of catalyst, solvent, and temperature on the polymerization of 2(9) are summarized in Table 4. Dioxane again is a poor solvent for the polymerization. While almost no polymer is obtained when the polymerization of 2(4) is catalyzed by WCl₆-Ph₄Sn in toluene at room temperature, under similar conditions 2(9) is polymerized into a polymer with an $M_{\rm w}$ of 13 100 in a moderate yield. Increasing the polymerization temperature leads to increments in both molecular weight and polymer yield. Similar to 2(4), the polymerization of 2(9) is hard to initiate by the MoCl₅-, NbCl₅-, and TaCl₅-Ph₄Sn mixtures.

Structural Characterization. The polymeric products were characterized by spectroscopic methods and all the polymers gave satisfactory data corresponding to their expected molecular structures (see Experimental Section for details). An example of the IR spectrum of P2(9) is shown in Figure 1; the spectrum of its monomer 2(9) is also given in the same figure for comparison. The monomer shows a weak band at 2230 cm⁻¹ associated with the C=C stretch (Figure 1A),



Figure 1. IR spectra of (A) monomer **2**(9) and (B) its polymer **P2**(9) (sample taken from Table 4, no. 3).



Figure 2. ¹H NMR spectra of chloroform-*d* solutions of (A) **2**(9) and (B) its polymer P**2**(9) (sample taken from Table 4, no. 3). The solvent peak is marked by an asterisk.

which completely disappears in the spectrum of its polymer (Figure 1B). The strong C=O band at 1715 cm⁻¹, however, experiences little change, proving that the acetylene polymerization is harmless to the carbonyl functional group.

The ¹H NMR spectra of P2(9) and its monomer 2(9) are shown in Figure 2. The protons of the phenyl ring next to the triple bond of 2(9) resonate at δ 7.40 and 7.28, which are upfield-shifted after the monomer is polymerized. No unexpected signals are observed in the spectrum of the polymer and all the resonance peaks can be assigned to appropriate protons as marked in Figure 2B. The NMR as well as the IR analyses confirm that the acetylene triple bond has been consumed by the polymerization reaction and that the molecular structure of the polymeric product is indeed P2(9), as given in Chart 1.



Figure 3. ¹³C NMR spectra of chloroform-*d* solutions of (A) **2**(9) and (B) its polymer P**2**(9) (sample taken from Table 4, no. 3). The solvent peaks are marked by asterisks.

Figure 3 shows the ¹³C NMR spectrum of **2**(9) along with that of its polymer P**2**(9). The acetylenic carbon atoms of **2**(9) resonate at δ 90.4 and 80.6. These absorptions are absent in the spectrum of P**2**(9). The resonance peaks of the acetylenic phenyl carbons at δ 131.5, 128.1, 127.4, and 124.1 and the propargyl carbon at δ 19.4 all disappear owing to the transformation of the acetylenic triple bonds to the olefinic double bonds by the acetylene polymerization. However, the absorptions of the olefinic carbons of the polyene backbone cannot be easily identified due to their overlapping with those of the pendant biphenyl carbons.

Thermal Stability and Liquid Crystallinity. Before investigating the mesomorphic properties of the polymers, we first examined their thermal stability. Poly(1-hexyne) (PH), a poly(1-alkyne), is so unstable that it starts to lose its weight when it is heated to a temperature as low as ~150 °C (Figure 4).²³ Polymers P1(*m*) and P2(*m*) are, however, thermally stable and lose almost no weight when they are heated to 360 °C in the thermogravimetric analysis (TGA). Clearly the incorporation of the stable biphenyl pendants into the polyacetylene structure has dramatically enhanced the thermal stability of the polymers, due to the protective "jacket effect" of the mesogenic groups⁹ plus the additional shielding effect contributed by the methyl or phenyl group directly attached to the polyene backbone.

Polymers P1(4), P1(9), and P2(9) exhibit optical anisotropy when heated or cooled but P2(4) does not, which suggests that the first three polymers are liquid crystalline but the fourth one is not. To know more about the thermal transitions of P1(*m*) and P2(9), their thermograms were measured under nitrogen on a differential scanning calorimeter (DSC). As can be seen from Figure 5A, P1(4) shows several transition peaks in the temperature range of 186.2-116.8 °C in the first cooling cycle. These thermal transitions are enantiotropic but their exact nature is difficult to identify. Their possible associations with cis-trans isomerization²⁴ and thermal degradation²³ can be ruled out. The molecular



Figure 4. TGA thermograms of P1(4) (sample taken from Table 1, no. 3), P1(9) (Table 2, no. 3), P2(4) (Table 3, no. 3), P2(9) (Table 4, no. 3), and poly(1-hexyne) (PH),²³ recorded under nitrogen at a heating rate of 20 °C/min.



Figure 5. DSC thermograms of mesomorphic polyacetylenes P1(4) (sample taken from Table 1, no. 3), P1(9) (Table 2, no. 3), and P2(9) (Table 4, no. 3) recorded under nitrogen during the (A) first cooling and (b) second heating scans at a scan rate of 10 °C/min.

weight of P1(4) does not change when it is heated to 200 °C, further proving that the chain scission and/or cross-linking reactions are not involved in the thermal transition processes. We are now working with our physicist colleagues in an effort to decipher the myths of these thermal transitions.

The polymer with nine methylene units, P1(9), readily forms the SmA mesophase enantiotropically. The melting and isotropization transitions of its biphenyl mesogens are well-defined. Its long alkyl spacer decouples the motions of the mesogenic pendant from the polyene backbone, enabling the mesogens to undergo thermal transitions in a relatively independent fashion. Similarly, P2(9) shows an enantiotropic smecticity. The



Figure 6. POM textures observed on cooling P1(4) (sample taken from Table 1, no. 3) to 128 °C (A), P2(9) (Table 2, no. 3) to 155 °C (B) and 135 °C (C), and P2(9) (Table 4, no. 3) to 168 °C (D) from their isotropic melts.

Table 5. Thermal Transitions and Corresponding Thermodynamic Parameters of P1(9) and P2(9)^a

	$T(\Delta H, \Delta X)$	S) ^b
polymer	cooling	heating
P 1 (9) P 2 (9)	i 157.3 (-7.95, -18.48) SmA 96.1 (-1.85; -5.24) g i 172.0 (-) SmA 158.6 (-10.21, -23.05) ^c g	g 99.0 (1.82, 4.89) SmA 163.6 (4.59, 10.51) i g 167.0 (11.35, 25.8) ^c SmA 188.3 (–) i

^{*a*} Data were taken from the DSC thermograms recorded under nitrogen in the first cooling and second heating scans. Abbreviations: n = nematic phase, SmA = smectic A phase, g = glassy state, i = isotropic melt. ^{*b*} T is given in degrees Celsius; ΔH is given in kilojoules per monomer repeating unit; ΔS is given in joules per monomer repeating unit per kelvin. ^{*c*} Sum of overlapping transitions.

temperature range for the smectic transition is, however, rather narrow, due to the high rigidity of its poly-(1-phenyl-1-alkyne) backbone. Indeed, this backbone is so stiff that it prevents P2(4), the congener of P2(9) with a shorter methylene spacer, from showing any mesomorphism.

Figure 6 shows microphotographs of the mesomorphic textures of P1(m) and P2(9) taken under a polarized optical microscope (POM). Upon cooling the isotropic liquid of P1(4), a birefringent texture is formed (Figure 6Å), the mesophasic nature of which is, however, difficult to specify. We repeatedly grew the liquid crystals with care but still failed to obtain any characteristic mesomorphic texture. The polymer with nine methylene units [P1(9)], however, readily forms the typical focal conic texture of SmA phase. Panels B and C of Figure 6 show the dynamic process of the texture formation. Many bâtonnets emerge from the dark background when P1(9) is cooled from its isotropic melt, which grow to bigger domains when the sample is further cooled. Further lowering the temperature encourages further growth of the domains, leading to the formation of the focal conic texture characteristic of the SmA phase. When P2(9) is cooled from its isotropic state, many anisotropic entities are formed but their development into the focal conic texture of SmA phase is difficult. The rigid poly(1-phenyl-1-alkyne) backbone

may have partially distorted the order of the mesogenic pendant groups and impeded them from growing into a characteristic SmA texture.

The thermal transitions of P1(9) and P2(9) and their corresponding enthalpy and entropy changes are summarized in Table 5.²⁵ The ΔH and ΔS for the i–SmA and SmA–i transitions of P1(9) are large, in agreement with the good packing order of its mesogens revealed by the POM observation (cf. Figure 6). Its mesomorphic temperature range is ~61 (i–g) or ~65 °C (g–i), which is much wider than that of P2(9) [~13 (i–g) or ~21 °C (g–i)]. It is known that an increase in the backbone rigidity of a polymer leads to a decrease in the stability of its liquid crystalline phase.²⁶ The observed difference in the mesomorphic temperature ranges between P1(9) and P2(9) agrees with the early observation that a poly-(2-alkyne) backbone is less stiff than a poly(1-phenyl-1-alkyne) one.²⁷

To gain more information on the mesomorphic structures of the polymers and their molecular packing arrangements in the mesomorphic phases, we measured their XRD data using the quenching technique developed in our early work.⁹ The diffractogram of P1(4) quenched from 128 °C shows a broad peak at 2θ = 20.35° (Figure 7), from which a *d* spacing of 4.36 Å is derived from Bragg's law (Table 6). No reflections are observed at low angles, indicating that there exists no

 Table 6. X-ray Diffraction Analysis Data of P1(4), P1(9), and P2(9)^a

polymer	<i>T</i> (°C)	d_1 (Å)	<i>d</i> ₂ (Å)	d_3 (Å)	<i>d</i> ₄ (Å)	mesogenic length ^b (<i>l</i> , Å)	ratio d_1/l	phase
P1(4)	128				4.36	25.16		n (?) ²⁹
P1(9)	140	32.10			4.40	31.38	1.02	SmA
P 2 (9)	170	32.70	16.51	11.11	4.33	31.38	1.04	SmA

^{*a*} The mesophases in the liquid crystalline states at given temperatures were frozen by rapid quenching with liquid nitrogen. ^{*b*} Calculated from monomer repeating units of the polymers in their fully extended conformations.



Figure 7. XRD patterns of the mesomorphic polyacetylenes quenched with liquid nitrogen from their liquid crystalline states: P1(4) (sample taken from Table 1, no. 3) at 128 °C, P2(9) (Table 2, no. 3) at 140 °C, and P2(9) (Table 4, no. 3) at 170 °C.

laver order. It is known that a nematic phase shows only a diffuse halo in a high angle region.²⁸ The optical anisotropy observed at 128 °C by POM may thus be associated with a nematic arrangement of the mesogens in P1(4).²⁹ The diffractogram of P1(9) displays a Bragg reflection at a low angle of $2\theta = 2.75^{\circ}$ and a large peak at a high angle of $2\theta = 20.15^\circ$. The *d* spacing derived from the low-angle peak is 32.10 Å, which is close to the calculated mesogenic length for the repeat unit of P1(9) at its most extended conformation (31.38 Å), thus proving the monolayer nature of the SmA phase. Similarly, P2(9) shows a reflection in the low-angle region, from which a *d* spacing of a monolayer SmA structure is derived. Interestingly, its secondary reflection at a middle angle of $2\theta = 5.35^{\circ}$ (16.51 Å) is also detected by the diffractometer. The peaks are, however, quite broad, suggesting that the mesogenic pendants are not well packed. The broad peak at $\tilde{2}\theta = \tilde{7}.95^{\circ}$ may be associated with the ordering of the biphenyl cores.⁹

Electronic Absorption and Light Emission. The absorption spectra of the tetrahydrofuran (THF) solutions of the polymers are given in Figure 8. Polymers P1(m) absorb strongly at 295 nm, which are assignable to the K bands of their biphenyl pendants, because their monomer absorptions peak at similar wavelengths. The polyene backbone absorptions of the polymers are, however, very weak. The low absorptivity of the poly-(2-alkyne) main chain may be due to the steric effect of the methyl group directly attached to the polyene backbone, which twists the double bonds and reduces the effective conjugation length along the main chain. The absorptions of the poly(1-phenyl-1-alkyne) backbone of P2(m) are, however, observed at wavelengths longer than 340 nm and extend up to ~425 nm. This suggests



Figure 8. UV spectra of THF solutions of P1(4) (sample taken from Table 1, no. 3), P1(9) (Table 2, no. 3), P2(4) (Table 3, no. 3), and P2(9) (Table 4, no. 3).



Figure 9. Photoluminescence spectra of THF solutions of P1(4) (sample taken from Table 1, no. 3), P1(9) (Table 2, no. 3), and poly(1-phenyl-1-octyne) (PPO). Polymer concentration was 0.05 mM. Excitation wavelengths were 335 nm [for P1(m)] and 355 nm (for PPO).

that the polymer backbone exists in a more planar conformation with a better conjugation. $^{\rm 30}$

A polymer with both liquid-crystalline and lightemitting properties may find unique technological applications,^{1–3,12} and we thus investigated the fluorescence properties of the polymers. When P1(4) is photoexcited at 335 nm, it emits a strong UV light of 369 nm (Figure 9). This UV emission is due to the photoluminescence (PL) of its biphenyl pendant, because the emission spectrum of its monomer 1(4) peaks at 366 nm. By use of 9,10-diphenylanthracene as reference, the fluorescence quantum yield (Φ_F) of P1(4) is calculated to be 69%. The PL of P1(9) is observed in the same spectral region with a higher emission efficiency (81%), in agreement with the previous observation that a



Figure 10. Photoluminescence spectra of THF solutions of **P2(**4) (sample taken from Table 3, no. 3), **P2(**9) (Table 4, no. 3), and PPO. Polymer concentration was 0.05 mM. Excitation wavelengths were (A) 335 and (B) 355 nm.

longer alkyl spacer favors stronger light emission.^{11,15} Poly(1-phenyl-1-octyne) {PPO; $-[(C_6H_5)C=C(C_6H_{13})]_n$ } is a well-known luminescent disubstituted polyacetylene, which emits a blue light of 460 nm with a quantum efficiency of 43% when its polyene backbone is photoexcited at 355 nm.¹⁵ Comparison with the PPO data reveals that the poly(2-alkyne) backbone of P1(*m*) does not emit in the visible region although their biphenyl pendants radiate efficiently in the UV region.

Polymers P2(*m*) are PPO derivatives bearing biphenyl pendants, and it is of interest to see how they emit upon photoexcitation. When excited at 335 nm, the biphenyl pendant of P2(4) emits weakly at 369 nm, with its PL spectrum dominated by a blue emission peaking at 460 nm (Figure 10A). As can be seen from the spectrum shown in Figure 8, the polyene backbone of P2(4)absorbs in a spectral region where its biphenyl pendant emits. Therefore, although the 335-nm excitation pumps its biphenyl pendant to the excited state, the UV light emitted from the pendant is reabsorbed by the polyene chromophore, hence explaining why the PL of the polymer is dominated by the blue emission of its backbone. The fluorescence spectrum of P2(9) is analogous to that of P2(4), suggesting that a similar energy transfer path is involved in the PL process of this polymer.

When excited by the photons of a longer wavelength (355 nm), P2(4) emits a blue light with a spectral profile similar to that given by the polymer when it is excited at the shorter wavelength (335 nm; cf. panels B and A of Figure 10). The quantum yield of the PL induced by the 355-nm excitation is 44%, which is much higher than that by the 335-nm excitation (9%) and comparable

to that of PPO (43%). While the 335-nm photons mainly excite the biphenyl pendant, the 355-nm photons can excite both the biphenyl pendant and the polyene backbone. The direct excitation plus the energy transferred from the pendant may be the cause for the more efficient emission of P2(4) induced by the longer wavelength excitation. The PL quantum yield of P2(9) is even higher (59%), once again demonstrating that the longer alkyl spacer promotes more efficient light emission.^{11,12,15}

Concluding Remarks

Following our previous success in polymerizing a special group of functional disubstituted acetylene monomers (namely, propiolates),18 in this work we succeeded in polymerizing two groups of "common" disubstituted acetylene monomers with no ester groups in the close neighborhood of the triple bonds, that is, the functional 2-alkynes [1(*m*)] and 1-phenyl-1-alkynes [2(m)]. This structural difference makes the new monomers behave quite differently from the propiolates: the former are polymerized by the tungsten catalyst; the latter, by the molybdenum one. The liquid crystallinity and light emission are realized in the new polymers with "right" molecular structures. The polymers with long alkyl spacers, viz., P1(9) and P2(9), exhibit thermotropic smecticity enantiotropically. Similar to the polypropiolates, the functional poly(2-alkyne) derivatives [P1(*m*)] emit UV light with high efficiency upon excitation of their biphenyl pendants. Backbone emission is achieved in the functional poly(1-phenyl-1-alkyne) system: P2(m)emit blue light when their pendants and/or backbones are excited. The long alkyl spacer is found to be good for both mesomorphism and luminescence. Its decoupling effect minimizes the influence of the rigid backbone on the packing of the mesogenic pendants^{7-9,12} and reduces the electronic interactions of the main and side chains, hence enabling efficient light emission.9-11,15,16

Experimental Section

Materials. Dioxane (Nacalai Tesque) and toluene (BDH) were 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. 4'-Heptyloxy-4-biphenylcarboxylic acid (6) was prepared according to our previously published procedures.⁹ Except for molybdenum(V) chloride (Acros), all other reagents and solvents were purchased from Aldrich and used without further purification.

Instrumentations. The IR spectra were measured on a Perkin-Elmer 16 PC Fourier transform infrared spectrophotometer. The NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer with 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 and the molar absorptivities (ϵ) of the polymers were calculated on the basis of their monomer repeating units. The mass spectra were recorded on a Finnigan TSQ 7000 triple-quadrupole mass spectrometer operating in a chemical ionization (CI) mode with methane as the carrier gas. The 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 a molecular weight range of $10^{3-}10^{7}$ was used for the molecular weight calibration.

The thermal stability of the polymers was evaluated by measuring their weight loss thermograms on a Perkin-Elmer TGA 7 under nitrogen at a heating rate of 20 °C/min. A Perkin-Elmer DSC 7 was used to measure the phase transition thermograms at a heating or cooling rate of 10 °C/min. An Olympus BX 60 POM equipped with a Linkam TMS 92 hot stage was used to observe anisotropic optical textures. The XRD patterns were recorded on a Philips PW1830 powder diffractometer with a graphite monochromator with 1.5406 Å Cu K α wavelength at room temperature (scanning rate 0.05 deg/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 reported in our previous papers.⁹

Monomer Synthesis. The 2-alkyne derivatives 1(m) were synthesized by esterification of 4'-heptyloxy-4-biphenylcarboxylic acid (**6**) with ω -alkyn-1-ol [**4**(m)] in the presence of 1,3dicyclohexylcarbodiimine (DCC), p-toluenesulfonic acid (TsOH), and 4-(dimethylamino)pyridine (DMAP) (Scheme 1). The 1-phenyl-1-alkyne derivatives 2(m) were prepared by esterification of the same acid with 1-phenyl-1-alkyn- ω -ol [**5**(m)], again with DCC as a dehydrating agent. Typical synthetic procedures are given below. (While all the compounds prepared in this work have been characterized spectroscopically, only the analysis data for the final products, i.e., the new monmers, are given below due to space limitations. The spectroscopic data for some of the intermediates can be found in handbooks, databases, etc.³¹)

5-Heptyn-1-ol [4(4)]. Into a two-necked 500-mL roundbottom flask equipped with a nitrogen inlet, a pressureequalized dropping funnel, and a magnet stirrer were added 100 mL of anhydrous THF and 3.6 g (37 mmol) of 5-hexyn-1ol [3(4)]. To this solution was added 35 mL (87.5 mmol) of 2.5 M solution of *n*-BuLi in pentane at -78 °C. The reaction was allowed to stay overnight and the mixture was then transferred into a separating funnel containing 200 mL of water and 100 mL of chloroform. The organic layer was separated and the aqueous phase was extracted with chloroform several times. The combined organic phase was washed with water and dried over anhydrous MgSO₄. The crude product was purified by vacuum distillation at 98 °C/21 mbar, and 5-heptyn-1-ol [4(4)] was obtained in 43.0% yield as a colorless liquid.

10-Dodecyn-1-ol [4(9)]. This compound was prepared by a procedure similar to that used for the synthesis of **4**(4) and was purified by vacuum distillation at 95 °C/1 mbar. Colorless liquid; yield 37.5%.

6-Phenyl-5-hexyn-1-ol [5(4)]. Into a 250-mL two-necked flask were added 0.6 g (0.9 mmol) of PdCl₂(PPh₃)₂, 0.2 mg (0.2 mmol) of CuI, and 180 mL of a triethylamine solution of iodobenzene (12.5 g, 61 mmol) under nitrogen. After all the catalysts were dissolved, 5-hexyn-1-ol [3(4); 4.5 g, 45 mmol] was injected into the flask and the mixture was stirred at room temperature for 24 h. After the formed salt was filtered out, the solution was concentrated by a rotary evaporator. The reaction product [5(4)] was purified on a silica gel column with chloroform/acetone (10:1 by volume) as the eluent. Yellow liquid; yield 92.0%.

11-Phenyl-10-undecyn-1-ol [5(9)]. This compound was prepared by a similar procedure. Yellow liquid; yield 90.7%.

7-{[(4'-Heptyloxy-4-biphenylyl)carbonyl]oxy}-2-heptyne [1(4)]. In a typical run, 4(4) (0.5 g, 4.9 mmol), DCC (1.5 g, 7.1 mmol), TsOH (0.2 g, 1.1 mmol), and DMAP (0.1 g, 0.8 mmol) were dissolved in 250 mL of dry dichloromethane in a 500-mL two-necked flask under nitrogen. The solution was cooled to 0-5 °C, to which 1.5 g of **6** (4.7 mmol) dissolved in 50 mL of dichloromethane was added under stirring via a dropping funnel. The reaction mixture was stirred overnight. After the formed urea solid was filtered out, the solution was concentrated by a rotary evaporator. The product was purified on a silica gel column with chloroform as the eluent. Recrystallization in an ethanol/H₂O mixture (4:1 by volume) gave monomer 1(4) as a white solid in 72.0% yield. Mp: 71.5 °C. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.07 (d, 2H, År-H ortho to CO₂), 7.61 (d, 2H, Ar-H meta to CO₂), 7.55 (d, 2H, Ar-H meta to OC₇H₁₅), 6.99 (d, 2H, Ar-H ortho to OC₇H₁₅), 4.35 (t, 2H, ArCO₂CH₂), 4.00 (t, 2H, OCH₂), 2.23 (m, 2H, ≡C-CH₂), 1.89–1.78 (m, 7H, CH₃C \equiv , ArCO₂CH₂CH₂, and \equiv CCH₂CH₂), 1.67 (m, 2 H, OCH₂CH₂), 1.36-1.32 [m, 8H, (CH₂)₄], 0.90 (t, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 166.5 (Ar CO₂), 159.4 (aromatic carbon linked with OC7H15), 145.2 (aromatic carbons para to CO₂), 132.1 (aromatic carbons para to OC₇H₁₅), 130.0 (aromatic carbons ortho to CO₂), 128.4 (aromatic carbons meta to OC₇H₁₅), 128.2 (aromatic carbon linked to CO₂), 126.3 (aromatic carbons meta to CO₂), 114.8 (aromatic carbons ortho to OC₇H₁₅), 78.6 (\equiv *C*CH₂), 76.0 (CH₃*C* \equiv), 68.1 (OCH₂), 64.5 (ArCO₂*C*H₂), 31.7, 29.2, 29.0, 27.9, 26.0, 25.6, 22.6, 18.4 (\equiv *C*-*C*H₂), 14.1, 3.4 (*C*H₃C \equiv). MS (CI): *m/e* 407.1 [(M + 1)⁺, calcd 407.1].

All other monomers used in this work were synthesized by procedures similar to that described above for the preparation of **1**(4). The characterization data for these monomers are given below:

12-{[(4'-Heptyloxy-4-biphenylyl)carbonyl]oxy}-2-dodecyne [1(9)]. Yield: 85.2%. White solid; mp 62.0 °C. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.07 (d, 2H, Ar–H ortho to CO₂), 7.61 (d, 2H, Ar-H meta to CO₂), 7.55 (d, 2H, Ar-H meta to OC7H15), 6.97 (d, 2H, Ar-H ortho to OC7H15), 4.32 (t, 2H, $ArCO_2CH_2$), 3.99 (t, 2H, OCH₂), 2.11 (m, 2H, \equiv C-CH₂), 1.83-1.76 (m, 9H, CH₃C≡, ArCO₂CH₂CH₂, ≡CCH₂CH₂, and OCH₂CH₂), 1.47-1.32 [m, 18H, (CH₂)₉], 0.90 (t, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 166.6 (ArCO₂), 159.4 (aromatic carbon linked to OC₇H₁₅), 145.1 (aromatic carbons para to CO₂), 132.1 (aromatic carbons para to OC₇H₁₅), 130.0 (aromatic carbons ortho to CO_2), 128.5 (aromatic carbons meta to OC7H15), 128.2 (aromatic carbon linked to CO2), 126.3 (aromatic carbons meta to CO₂), 114.9 (aromatic carbons ortho to OC₇H₁₅), 79.3 ($\equiv CCH_2$), 75.3 (CH₃C \equiv), 68.1 (OCH₂), 65.0 (ArCO₂CH₂), 31.7, 29.4, 29.23, 29.22, 29.1, 29.0, 28.8, 28.7, 26.0, 22.6, 18.7 ($\equiv C - CH_2$), 14.1, 3.4 ($CH_3C \equiv$). MS (CI): m/e 477.2 [$(M + 1)^+$, calcd 477.2].

6-{[(4'-Heptyloxy-4-biphenylyl)carbonyl]oxy}-1-phenyl-1-hexyne [2(4)]. Yield: 85.7%. White solid; mp 75.0 °C. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.08 (d, 2H, Ar–H ortho to CO₂), 7.61 (d, 2H, Ar-H meta to CO₂), 7.54 (d, 2H, Ar-H meta to OC_7H_{15}), 7.40 (m, 2H, Ar-H ortho to C=C), 7.26 (m, 3H, Ar-H para and meta to C=C), 6.97 (d, 2H, Ar-H ortho to OC7H15), 4.39 (t, 2H, ArCO2CH2), 3.99 (t, 2H, OCH2), 2.51 (m, 2H, \equiv C-CH₂), 1.98 (m, 2H, ArCO₂CH₂CH₂), 1.80 (m, 4H, \equiv CCH₂CH₂ and OCH₂CH₂), 1.49–1.32 [m, 8H, (CH₂)₄], 0.90 (t, 3H, CH₃). ^{13}C NMR (75 MHz, CDCl₃), δ (ppm): 166.5 $(ArCO_2)$, 159.4 (aromatic carbon linked to OC_7H_{15}), 145.2 (aromatic carbons para to CO₂), 132.0 (aromatic carbons para to OC_7H_{15}), 131.5 (aromatic carbons ortho to C=C), 130.0 (aromatic carbons ortho to CO₂), 128.3 (aromatic carbons meta to OC7H15), 128.2 (aromatic carbon linked to CO2), 128.1 (aromatic carbons meta to C=C), 127.5 (aromatic carbons para to C=C), 126.3 (aromatic carbons meta to CO_2), 123.8 (aromatic carbon linked to C=C), 114.8 (aromatic carbons ortho to OC_7H_{15}), 89.5 (=*C*CH₂), 81.1 (Ar*C*=), 68.0 (OCH₂), 64.4 (ArCO₂*C*H₂), 31.7, 29.2, 29.0, 27.9, 25.9, 25.3, 22.5, 19.1 (≡C- CH_2 , 14.0. MS (CI): m/e 469.1 [(M + 1)⁺, calcd 469.1].

11-{[(4'-Heptyloxy-4-biphenylyl)carbonyl]oxy}-1-phenyl-1-undecyne [2(9)]. Yield: 88.1%. White solid; mp 55.0 °C. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.09 (d, 2H, Ar–H ortho to CO₂), 7.63 (d, 2H, Ar-H meta to CO₂), 7.57 (d, 2H, Ar-H meta to OC_7H_{15}), 7.40 (m, 2H, Ar-H ortho to C=C), 7.28 (m, 3H, Ar-H para and meta to C \equiv C), 7.00 (d, 2H, Ar-H ortho to OC7H15), 4.37 (t, 2H, ArCO2CH2), 4.01 (t, 2H, OCH2), 2.42 (m, 2H, \equiv C-CH₂), 1.81 (m, 4H, ArCO₂CH₂CH₂ and ≡CCH₂CH₂), 1.68 (m, 2H, OCH₂CH₂), 1.48-1.34 [m, 18H, $(CH_2)_9$], 0.92 (t, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 166.6 (ArCO₂), 159.4 (aromatic carbon linked to OC₇H₁₅), 145.1 (aromatic carbons para to CO₂), 132.2 (aromatic carbons para to OC₇H₁₅), 131.5 (aromatic carbons ortho to C=C), 130.0 (aromatic carbons ortho to CO_2), 128.5 (aromatic carbons meta to OC₇H₁₅), 128.3 (aromatic carbon linked to CO₂), 128.1 (aromatic carbons meta to C=C), 127.4 (aromatic carbons para to C \equiv C), 126.3 (aromatic carbons meta to CO₂), 124.1 (aromatic carbon linked to C=C), 114.9 (aromatic carbons ortho to OC_7H_{15}), 90.4 (=*C*CH₂), 80.6 (Ar*C*=), 68.1 (OCH₂), 65.0 (ArCO₂CH₂), 31.8, 29.4, 29.25, 29.23, 29.1, 28.8, 28.7, 26.02, 26.00, 22.6, 19.4 (=C-CH₂), 14.1. MS (CI): m/e 539.3 $[(M + 1)^+, calcd 539.3].$

Polymerization. All the polymerization reactions and manipulations were carried out under nitrogen by Schlenk

techniques in a vacuum line system or a Vacuum Atmospheres inert-atmosphere glovebox, except for the purification of the polymers, which was done in an open atmosphere. A typical experimental procedure for the polymerization of 1(4) is given below as an example.

Into a baked 20-mL Schlenk tube with a stopcock in the sidearm was added 257.0 mg (0.63 mmol) of 1(4). The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the sidearm. Freshly distilled toluene (1.5 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 12.0 mg of tungsten(VI) chloride and 13.0 mg of tetraphenyltin in 1.5 mL of toluene. The catalyst solution was aged at 60 °C for 15 min, to which the monomer solution was added by use of 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 was then filtered with a Gooch crucible. The polymer [P1(4)] was washed with acetone and dried in a vacuum oven to a constant weight.

Characterization Data: P1(4). Grey powder; yield 81.4%. M_w 254 200; M_w/M_n 2.0 (GPC; Table 1, no. 3). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.94, 7.41, 6.97 (Ar–H), 4.34 (ArCO₂CH₂), 3.86 (OCH₂), 1.74 (ArCO₂CH₂CH₂ and =CCH₂CH₂), 1.31 [(CH₂)₅], 0.90 (CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 166.3 (ArCO₂), 159.3 (aromatic carbon linked to OC₇H₁₅), 144.8 (aromatic carbons para to CO₂), 131.9 (aromatic carbons para to OC₇H₁₅), 130.0 (aromatic carbons ortho to CO₂), 128.1 (aromatic carbons meta to OC₇H₁₅ and linked to CO₂), 126.1 (aromatic carbons meta to CO₂), 114.7 (aromatic carbons ortho to OC₇H₁₅), 68.0 (OCH₂), 64.8 (ArCO₂CH₂), 31.8, 29.3, 29.1, 26.0, 22.6, 14.1. UV (THF, 7.4 × 10⁻⁵ mol/L): λ_{max} 295 nm, ϵ_{max} 2.02 × 10⁴ mol⁻¹ L cm⁻¹.

P1(9). Grey powder; yield 80.7%. M_w 22 600; M_w/M_n 8.9 (GPC; Table 2, no. 3). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.99, 7.48, 6.88 (Ar–H), 4.25 (ArCO₂CH₂), 3.90 (OCH₂), 1.92 (ArCO₂CH₂CH₂, =CCH₂CH₂, and OCH₂CH₂), 1.30 [(CH₂)₉], 0.88 (CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 166.4 (ArCO₂), 159.3 (aromatic carbon linked to OC₇H₁₅), 144.9 (aromatic carbons para to CO₂), 131.9 (aromatic carbons para to OC₇H₁₅), 129.9 (aromatic carbons ortho to CO₂), 128.4 (aromatic carbons meta to OC₇H₁₅), 1278.1 (aromatic carbon linked to CO₂), 126.2 (aromatic carbons meta to CO₂), 114.7 (aromatic carbons ortho to OC₇H₁₅), 67.9 (OCH₂), 64.9 (ArCO₂CH₂), 31.7, 29.2, 29.0, 28.7, 25.9, 22.5, 14.0. UV (THF, 5.9 × 10⁻⁵ mol/L): λ_{max} 295 nm, ϵ_{max} 1.99 × 10⁴ mol⁻¹ L cm⁻¹.

P2(4). Grey powder; yield 63.2%. M_w 63 000; M_w/M_n 1.9 (GPC; Table 3, no. 3). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.84, 7.41, 6.84 (Ar–H), 3.88 (ArCO₂CH₂ and OCH₂), 1.74 (ArCO₂CH₂CH₂, =CCH₂CH₂, and OCH₂CH₂), 1.31 [(CH₂)₄], 0.89 (CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 166.1 (ArCO₂), 159.2 (aromatic carbon linked to OC₇H₁₅), 144.6 (aromatic carbons para to CO₂), 131.9 (aromatic carbons para to OC₇H₁₅), 129.9 (aromatic carbons ortho to CO₂), 128.1 (aromatic carbons meta to OC₇H₁₅ and linked to CO₂), 126.1 (aromatic carbons meta to CO₂), 114.7 (aromatic carbons ortho to OC₇H₁₅), 67.9 (OCH₂), 64.3 (ArCO₂CH₂), 31.8, 29.2, 29.1, 26.0, 22.6, 14.1. UV (THF, 7.3 × 10⁻⁵ mol/L): λ_{max} 295 nm, ϵ_{max} 2.44 × 10⁴ mol⁻¹ L cm⁻¹.

P2(9). Yellow powder; yield 48.7%. M_w 43 900; M_w/M_n 2.1 (GPC; Table 4, no. 3). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.00, 7.50, 6.90 (Ar–H), 4.26 (ArCO₂C*H*₂), 3.93(OCH₂), 1.76 (ArCO₂CH₂C*H*₂ and =CCH₂C*H*₂), 1.31 [(CH₂)₁₀], 0.89 (CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 166.4 (Ar*C*O₂), 159.3 (aromatic carbon linked to OC₇H₁₅), 144.9 (aromatic carbons para to CO₂), 132.0 (aromatic carbons para to OC₇H₁₅), 128.1 (aromatic carbon linked to CO₂), 128.4 (aromatic carbons meta to OC₇H₁₅), 128.1 (aromatic carbon linked to CO₂), 126.2 (aromatic carbons meta to CO₂), 114.8 (aromatic carbons ortho to OC₇H₁₅), 68.0 (OCH₂), 64.9 (ArCO₂*C*H₂), 31.7, 29.2, 29.0, 28.8, 25.9, 22.5, 14.0. UV (THF, 7.1 × 10⁻⁵ mol/L): λ_{max} 295 nm, ϵ_{max} 2.28 × 10⁴ mol⁻¹ L cm⁻¹.

Acknowledgment. The work described in this paper was partially supported by the Research Grants Council (Projects N_HKUSR606_03, 604903, HKUST6085/02P, 6121/01P, and 6187/99P) and the University Grants Committee of Hong Kong through an Area of Excellence (AoE) Scheme (Project AoE/P-10/01-1A).

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MA049094D