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Disubstituted Polyacetylenes Containing Photopolymerizable Vinyl Groups and Polar Ester Functionality: Polymer Synthesis, Aggregation-Enhanced Emission, and Fluorescent Pattern Formation

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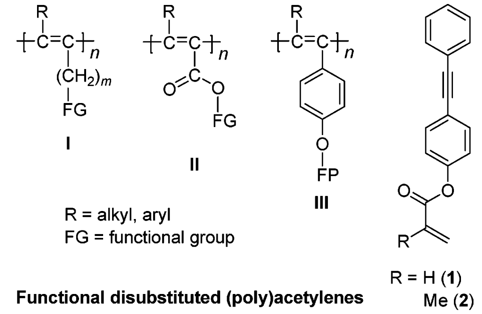
ABSTRACT: Diphenylacetylene monomers functionalized with vinyl and ester groups (**1** and **2**) were synthesized. The monomers were polymerized by WCl_6-Ph_4Sn into their corresponding polymers (P**1** and P**2**) with the (meth)-acrylic functionality remained intact, as verified by the structural analysis of the polymers using spectroscopic methods. The polymers are soluble in common organic solvents and form films of good quality when their solutions are spin-coated. The solutions of the polymers emit green light upon photoexcitation. Their emission spectra shift to longer wavelengths and narrow in widths when the solution concentrations are increased, presumably due to the formation of the intramolecular excimers. When the polymer chains are aggregated, their emission efficiencies are increased (Φ_F up to ~88%), showing a unique phenomenon of aggregation-enhanced emission. The (meth)acrylic groups bestow photosensitivity on the polymers, whose photo-cross-linking enables ready fabrication of highly fluorescent photoresist patterns.

Introduction

The successful preparation of polyacetylene (PA) films and the discovery of metallic conductivity of their doped forms have opened up a new area of research on "synthetic metals" or "plastic electronics".[1] PA is, however, instable and intractable. Thanks to the synthetic efforts of polymer chemists in the area, various strategies and approaches have been developed to improve the stability and processability of PA.[2−4] Substituted PAs $\{-[(R)C{=}C(R')]-\}$ can be more stable and soluble than their parent form if the R/R′ groups are properly chosen.[5] When the substituents are bulky groups, the resultant PAs often show high thermal stability, good solubility, and excellent film-forming capability.[5] A large number of monosubstituted PAs bearing various pendant groups have been designed and synthesized.[4−17] When appropriate pendants are introduced, the polymers can be endowed with such functional properties as mesomorphism,[4,6] luminescence,[5,7−9] photoconductivity,[10] redox activity,[11,12] gas permeability,[13] chain helicity,[14−16] biocompatibility, and cytophilicity.[17]

Despite these attractive functionalities, monosubstituted PAs still suffer from the instability problem: many of them degrade during storage, especially in the solution state. The polymers are easily oxidized when the solutions are exposed to air, as evidenced by the decreases in their molecular weights. These disadvantages limit the scope of their potential technological applications. In contrast, disubstituted PAs are often thermally stable and mechanically strong.[4,17−19] Furthermore, they commonly emit strong lights upon photoexcitation, showing fluorescence quantum yields (Φ_F) up to 98%.[4,19,20] Syntheses of disubstituted PAs have, however, been difficult. It is even more challenging to polymerize disubstituted acetylenes containing polar functional groups. Transition-metal compounds such as $TaCl_5$ and $NbCl_5$ are the best-known catalysts for the polymerization of nonpolar disubstituted acetylenes[4,21] but are intolerant of functional groups. An important task in the area is thus to develop catalyst systems that can polymerize disubstituted acetylenes containing various functional groups.

Chart 1. Functional Disubstituted (Poly)acetylenes



We have previously succeeded in polymerizing some disubstituted acetylenes containing functional groups such as **I**−**III** given in Chart 1.[4] In this work, we tried to polymerize disubstituted acetylenes with vinyl groups attached to a diphenylacetylene skeleton via ester bridges (**1** and **2**). The monomers are comprised of two functional units: diphenylacetylene and (meth)acrylate. The former will make their polymers, if successfully polymerized, highly luminescent, while the latter will make the polymers readily photo-cross-linked. Polymerizations of such bifunctional monomers with similar structures were previously attempted using the Grubbs−Hoveyda ruthenium complex as catalyst, but the highest polymer yield was merely 5%.[22] In this work, using a simple mixture of WCl_6-Ph_4Sn as

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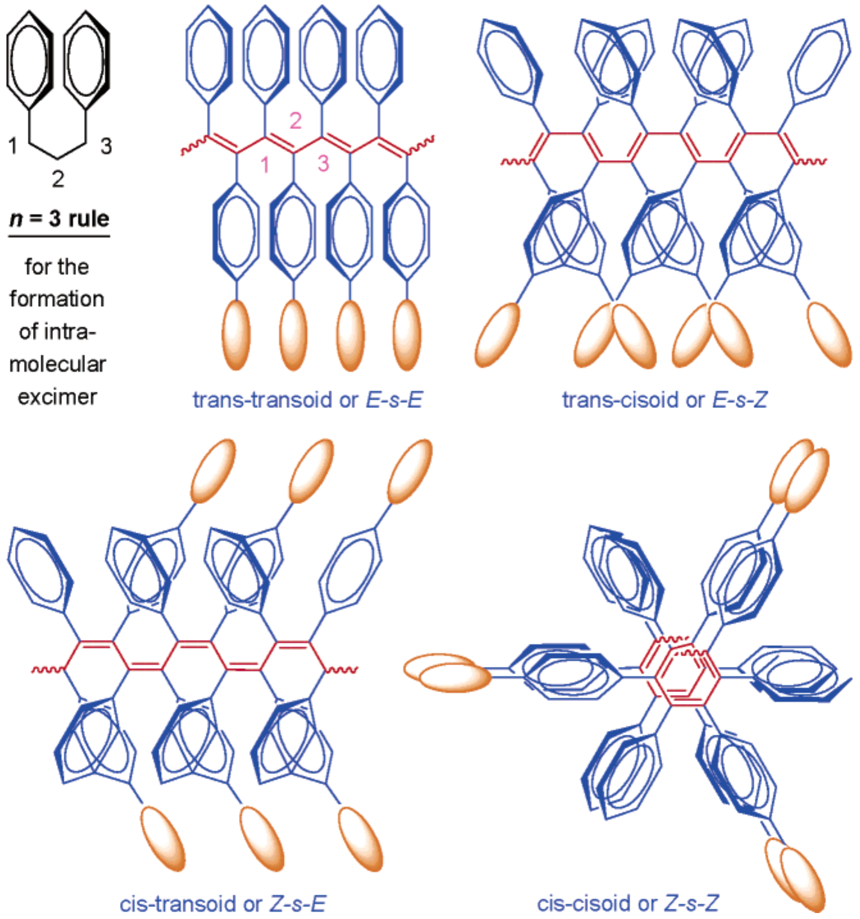
Chart 2



catalyst, we polymerized the monomers into their polymers in much higher yields (up to 25%).

Experimental Section

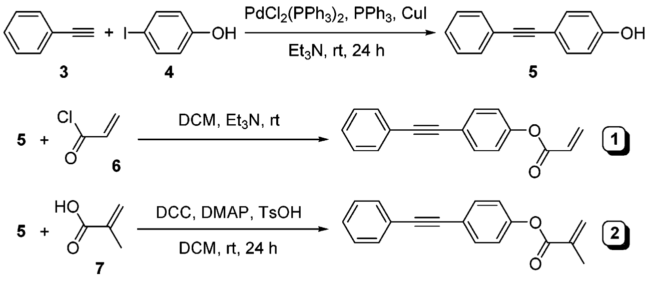
Materials. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under argon immediately prior to use. Toluene and dichloromethane (DCM) were distilled from calcium hydride. Triethylamine was distilled and dried over potassium hydroxide. Other solvents of high purities were used without further purification. 4-(Dimethylamino)pyridine (DMAP; Aldrich), *N*,*N*′-dicyclohexylcarbodiimide (DCC; SCRC), *p*-toluenesulfonic acid monohydrate (TsOH; Aldrich), copper(I) iodide (SCRC), triphenylphosphine (SCRC), dichlorobis(triphenylphosphine)palladium(II) (Aldrich), 4-iodophenol (Aldrich), phenylacetylene (Aldrich), acryloyl chloride (Aldrich), methacrylic acid (SCRC), tungsten(VI) chloride (Aldrich), tetraphenyltin (ABCR), and *n*-tetrabutyltin (Aldrich) were all of analytical grades and used as received.

Instrumentation. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 500 spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. IR spectra were recorded on a Bruker VECTOR 22 spectrometer. UV−vis absorption spectra were measured on a Varian CARY 100 Bio spectrophotometer. Thermal stability of the polymers was evaluated on a Perkin-Elmer Pyris thermogravimetric analyzer TGA 6. Fluorescence spectra were recorded on a Perkin-Elmer spectrofluorometer LS 55. Fluorescence quantum yields (Φ_F's) were estimated using Rhodamine B as reference ($\Phi_F = 97\%$ in ethanol). Weight (M_w)- and number-average (M_n) molecular weights and polydispersity indexes (M_w/M_n) of the polymers were estimated in THF by a Waters Associated gel permeation chromatography (GPC) system. A set of monodisperse polystyrene standards covering molecular weight range of 10^3-10^7 was used for the molecular weight calibration.

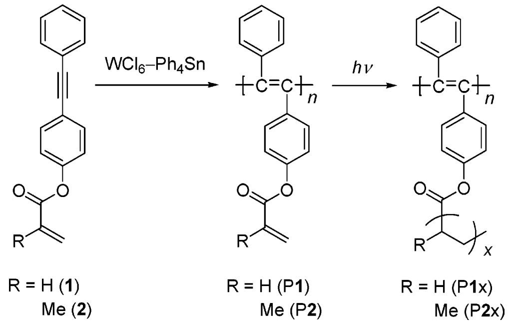
Monomer Synthesis. As shown in Scheme 1, the disubstituted acetylene monomers were prepared by a coupling reaction between phenylacetylene (**3**) and 4-iodophenol (**4**) followed by the esterification of the intermediate (**5**) with acryloyl chloride (**6**) and methacrylic acid (**7**). Given below are the typical experimental procedures for the syntheses of the monomers, namely, 4-(phenylethynyl)phenyl acrylate (**1**) and 4-(phenylethynyl)phenyl methacrylate (**2**).

Preparation of 4-(Phenylethynyl)phenol (5). Into a 500 mL two-necked flask were added 175.0 mg (0.25 mmol) of $PdCl_2(PPh_3)_2$, 95.0 mg (0.5 mmol) of CuI, 66.0 mg (0.25 mmol) of PPh_3, and 150 mL of a triethylamine solution of **4** (5.5 g, 25 mmol) under nitrogen. After all the catalysts were dissolved, 3.6 mL of **3** (32.5 mmol) in 50 mL of triethylamine was injected into the flask. The mixture was stirred at room temperature for 24 h. After the formed salt was filtered out, the solution was concentrated with a rotary evaporator. The crude product was purified by a silica gel column using a chloroform/hexane (3:2 by volume) mixture as eluent. Light brown solid was isolated in 86.2% yield. IR (KBr), ν (cm^{-1}): 3382 (s, −OH), 2216 (s, C≡C). ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.5 (m, 2H), 7.4 (m, 2H, aromatic protons *meta* to −O−),

Scheme 1



Scheme 2



7.3 (m, 3H), 6.8 (m, 2H, aromatic protons *ortho* to −O−), 5.1 (s, 1H, −O*H*).

*Synthesis of 4-(Phenylethynyl)phenyl Acrylate (**1**).* Into a 100 mL two-necked, round-bottom flask were added 1.5 mL (15 mmol) of **6** and 40 mL of DCM. The flask was cooled using an ice−water bath. A solution of **5** (1.94 g, 10 mmol) in 20 mL of DCM was injected. The mixture was slowly warmed to room temperature and stirred overnight. After filtering out the formed salt, the solvent was distilled off using a rotary evaporator. The crude product was purified by a silica gel column using a mixture of chloroform/hexane (1:1 by volume) as eluent. White solid of **1** was isolated in 70.5% yield. IR (KBr), ν (cm^{-1}): 2218 (s, C≡C), 1735 (s, C═O). ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.5 (m, 4H), 7.3 (m, 3H), 7.1 (m, 2H, aromatic protons *ortho* to −O−), 6.6 (m, 1H), 6.3 (m, 1H, −OOCC*H*), 6.0 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 164.4 (*C*═O), 150.6 (aromatic carbon *ortho* to −O−), 131.7 (−CH═*C*H$_2$), 127.8 (−*C*H═CH$_2$), 132.8, 128.5, 121.8, 123.3, 121.1 (aromatic carbons), 89.6 (Ph*C*≡CPh), 88.6 (PhC≡*C*Ph).

*Synthesis of 4-(Phenylethynyl)phenyl Methacrylate (**2**).* Into a 250 mL round-bottom flask were placed 1.94 g (10 mmol) of **5**, 1.0 g (12 mmol) of **7**, 3.0 g of DCC, 245 mg of DMAP, and 380 mg of TsOH in 150 mL of DCM. The resulting mixture was stirred at room temperature for 24 h. After filtering the formed urea salts, the solid was washed with diethyl ether. The filtrate was concentrated using a rotary evaporator. The crude product was purified by a silica gel column using a mixture of chloroform/hexane (1:1 by volume) as eluent. A white solid was obtained in 90.2% yield. IR (KBr), ν (cm^{-1}): 2217 (s, C≡C), 1736 (s, C═O). ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.5 (m, 4H, aromatic protons *ortho* to C≡C), 7.3 (m, 3H),7.1 (m, 2H, aromatic protons *ortho* to −O−), 6.4 (s, 1H), 5.8 (s, 1H), 2.1 (s, 3H, −CH$_3$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 166.2 (C═O), 151.4 (aromatic carbon *ortho* to −O−), 136.4 (−C═*C*H$_2$), 128.2 (−*C*═CH$_2$), 133.4, 132.3, 129.0, 123.8, 122.4, 121.5 (aromatic carbons), 90.1 (Ph*C*≡CPh−), 89.3 (PhC≡*C*Ph−), 19.0 (−CH$_3$).

Polymerization Reactions. The monomers were polymerized using a WCl_6−Ph_4Sn mixture as catalyst (Scheme 2). The polymerization reactions and manipulations were carried out under nitrogen using an inert atmosphere glovebox, except for the purification of the polymers, which was done in a fume hood. A typical experimental procedure for the polymerization of monomer **1** is given below as an example.

Into a baked 20 mL Schlenk tube was added 195.0 mg (0.8 mmol) of **1**. The tube was evacuated under vacuum in a glovebox for half an hour and then flushed with nitrogen. 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 17.1 mg of tetraphenyltin in 2 mL of toluene. The catalyst solution was aged at 80 °C for 15 min, into which the monomer solution was added using a hypodermic syringe. The reaction mixture was stirred at 80 °C 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 methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight, which was then filtered with a Gooch crucible. Product P**1** was isolated by washing it with a methanol/acetone (3:1 by volume) mixture and drying in a vacuum oven at 40 °C to a constant weight. IR (KBr), ν (cm^{-1}): 1736 (C═O). ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 6.73, 6.52 (aromatic protons and one proton of C*H*$_2$), 6.2 (C*H*═CH$_2$), 5.9 (one proton of C*H*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 163.9 (*C*═O), 150.6 (aromatic carbon *ortho* to −O−), 146.4, 144.9 (carbons of olefinic double bond in the main chain), 142.9, 141.1 (aromatic carbons *ortho* to the main chain), 131.6 (−CH═*C*H$_2$), 128.3, 126.8, 126.2, 125.6 (aromatic carbons), 119.1 (−*C*H═CH$_2$).

Table 1. Polymerization of Diphenylacetylene Derivatives Containing (Meth)acrylic Moieties[a]

no.	catalyst	temp (°C)	time (h)	yield (%)	M_w[b]	M_w/M_n[b]
	4-(Phenylethynyl)phenyl Acrylate (**1**)					
1	$TaCl_5$−*n*-Bu_4Sn	80	24	0		
2	WCl_6−*n*-Bu_4Sn	80	24	0		
3	WCl_6−Ph_4Sn	80	24	14.0	11200	1.5
4	WCl_6−Ph_4Sn	80	48	9.0	7500	1.3
5	WCl_6−Ph_4Sn	100	24	20.5	13700	1.9
6	WCl_6−Ph_4Sn	100	72	18.0	8500	1.3
	4-(Phenylethynyl)phenyl Methacrylate (**2**)					
7	WCl_6−Ph_4Sn	80	24	22.5	9100	1.4
8	WCl_6−Ph_4Sn	100	24	25.0	9400	1.4

[a] Carried out under nitrogen in toluene; $[M]_0 = 0.2$ M, [cat.] = 10 mM, [*n*-Bu_4Sn] = 20 mM, [Ph_4Sn] = 10 mM. [b] Estimated by GPC in THF on the basis of a polystyrene calibration.

Polymer P**2** was synthesized from the polymerization of **2** catalyzed by WCl_6−Ph_4Sn using the similar experimental procedures. IR (KBr), ν (cm^{-1}): 1736 (C═O). ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.0, 6.9, 6.5 (aromatic protons and one proton of C*H*$_2$), 5.9 (one proton of C*H*$_2$), 2.2 (−CH$_3$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 165.8 (C═O), 152.2 (aromatic carbon *ortho* to −O−), 149.5, 146.6 (carbons of olefinic double bond in the main chain), 143.6, 141.9 (aromatic carbons *ortho* to the main chain), 136.9, 136.4, 132.2, 129.0, 127.1, 126.2, 125.5, 119.7, 19.2 (−*C*H$_3$).

Fluorescent Photopatterning. Photo-cross-linking reactions of the polymer films were carried out using a 365 nm light obtained from a Spectroline ENF-280C/F UV lamp. The intensity of the incident light was 32 mW/cm^2. The films were prepared by spin-coating the polymer solutions (5 mg/mL in 1,2-dichloroethane) at 500 rpm for 9 s and then 2000 rpm for 1 min on silicon wafers. The films were dried in vacuum at 40 °C overnight. The photoresist patterns were prepared on the silicon wafers using Cu-negative masks. After UV exposure, the films were developed in 1,2-dichloroethane for 60 s at room temperature and then dried for 3 h at 40 °C under reduced pressure. Fluorescent images of the resulting patterns were taken on an Olympus BX41 fluorescent optical microscope.

Results and Discussion

Polymer Synthesis. To polymerize monomers **1** and **2**, we tried different catalyst systems. $TaCl_5$ and $NbCl_5$ are the most widely used catalysts for the polymerizations of disubstituted acetylenes. We first attempted to use $TaCl_5$ as catalyst and Bu_4Sn as cocatalyst to polymerize **1**. Stirring a mixture of $TaCl_5$−Bu_4Sn and **1** in toluene at 80 °C for 24 h under nitrogen, however, gives a disappointing result with no polymer formed at all (Table 1, no. 1). Thus, $TaCl_5$ has no catalytic effect on the polymerization of **1**. This confirms the intolerance of $TaCl_5$ to functional groups in disubstituted acetylene monomers. Previously, we have found that WCl_6−Bu_4Sn is tolerant of certain functional groups.[4] We thus tried to use WCl_6 to replace $TaCl_5$ to do the polymerization of **1** under the same reaction conditions. No polymeric product is obtained from this system either: evidently the combination of WCl_6 and Bu_4Sn is incapable of initiating the polymerization of **1.** We then tried a WCl_6−Ph_4Sn mixture, which has been found to be able to

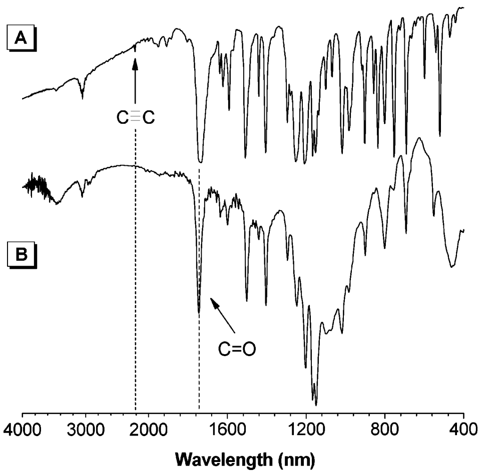


Figure 1. IR spectra of (A) monomer **1** and (B) its polymer P**1**.

initiate polymerizations of some functional disubstituted acetylenes.[4] Delightfully, polymer is formed in the presence of this catalyst system (Table 1, no. 3)! The failure of WCl_6-Bu_4Sn and the success of WCl_6-Ph_4Sn testify a pronounced "cocatalyst effect" in the polymerization of **1**.

According to our experience in the area, temperature exerts a great influence on the polymerization of disubstituted acetylenes. At room temperature, the reaction is normally sluggish and the polymer yield is usually low. A higher temperature often makes the catalyst more active and thus greatly accelerates the polymerization reaction.[23] We investigated how the temperature would affect the polymerization of **1**. The reaction carried out at 100 °C affords a polymer yield much higher than that at 80 °C (cf. Table, 1, nos. 3 and 5). The temperature elevation thus exerts a positive effect on the polymerization of **1**. The obtained polymer is completely soluble in common organic solvents such as chloroform, DCM, THF, and toluene. When the reaction is conducted at a higher temperature, e.g., at the boiling point of toluene, the resultant polymer becomes insoluble. This suggests that, when the temperature is ≤100 °C, the vinyl double bond of the acrylic moiety remains unreacted when the acetylene triple bond undergoes metathesis polymerization. In other words, the triple bond of **1** is selectively polymerized by the WCl_6-Ph_4Sn catalyst.

In an effort to further enhance the polymer yield, we designed and synthesized monomer **2**, whose polar ester group is "shielded" by a bigger methyl group. It is hoped that the methacrylic moiety in **2** will irritate the transition-metal catalyst to a less extent than its acrylic counterpart in **1**. This proves to be the case: the polymerizations of **2** by the WCl_6-Ph_4Sn mixture at 80 and 100 °C produce polymers in higher yields (Table 1, nos. 7 and 8) than those of **1** under the similar conditions (Table 1, nos. 3 and 5).

Structure Characterization. The polymeric products were characterized spectroscopically. All the polymers give satisfactory analysis data corresponding to their expected molecular structures (see Experimental Section for details). An IR spectrum of P**1** is shown in Figure 1 as an example, with that of its monomer (**1**) given in the same figure for comparison. The monomer shows an absorption band at 2222 cm^{-1} associated with C≡C stretching. This band is not observed in the spectrum of P**1**. On the other hand, the band at 1740 cm^{-1} associated with C═O stretching is clearly seen in the spectrum of the polymer. These results indicate that monomer **1** has been successfully transformed to polymer P**1** with its ester functionality remained intact.

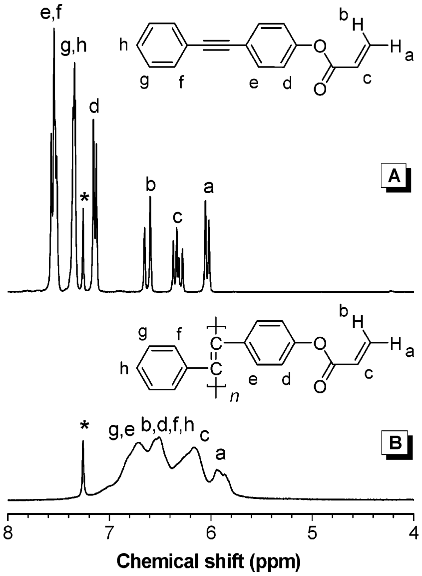


Figure 2. ^1H NMR spectra of (A) monomer **1** and (B) its polymer P**1** in chloroform-*d*. The solvent peaks are marked with asterisks.

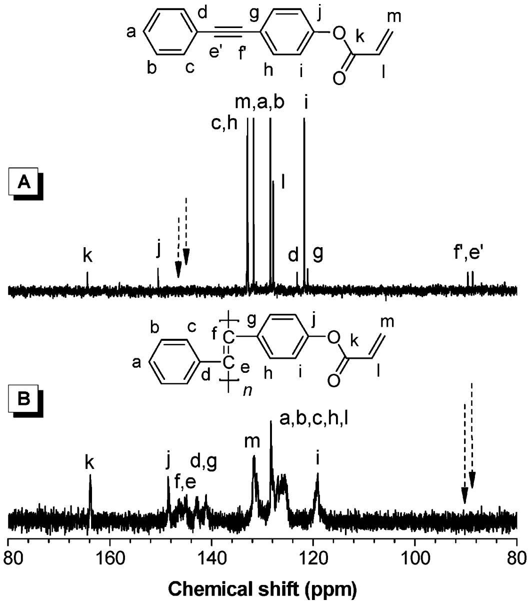


Figure 3. ^{13}C NMR spectra of (A) monomer **1** and (B) its polymer P**1** in chloroform-*d*.

Figure 2 shows the ^1H NMR spectra of P**1** and its monomer **1**. The protons of the two phenyl rings of monomer **1** resonate at δ 7.13, 7.33, and 7.51 (labeled as d, e, f, g, and h), which are absent in the spectrum of its polymer (P**1**). The polymerization reaction has transformed the acetylenic triple bond of **5** to olefinic double bond. This shifts the resonances of the phenyl protons to the upfield, which now occur at δ 6.54 and 6.72 (Figure 2B). Much less change is seen in the resonance peaks of the acrylic protons because they are located far away from the polyene backbone. No unexpected peaks are observed in the spectra of the monomer and the polymer: all the peaks can be readily assigned to the resonances of appropriate protons as marked in Figure 2. This confirms that the W-based catalyst has selectively polymerized the acetylene unit of monomer **1**: the triple bonds have been consumed by the polymerization, while the acrylic functionality has been left unharmed.

The ^{13}C NMR spectra of P**1** and **1** are shown in Figure 3. The acetylene carbon atoms of **1** resonate at δ 88.7 (f′) and 89.6 (e′); these peaks are completely absent in the spectrum of

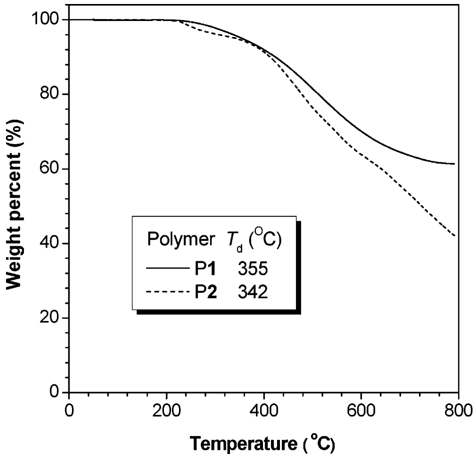


Figure 4. TGA thermograms of P**1** and P**2** recorded under nitrogen at a heating rate of 10 °C /min.

P**1**. Instead, two new peaks appear at δ 144.9 (f) and 146.4 (e), which are assignable to the resonances of carbon atoms in the polyene backbone of P**1**. This again proves that the polymerization is realized via the transformation of triple bond to double bond. Since the phenyl rings conjugate electronically with the PA backbone, the resonance of the phenyl carbon atoms directly attached to the double bond (d and g) have downfield shifted from δ 123.2 and 121.1 to δ 142.8 and 141.0, respectively. All other peaks in the spectra of the monomer and the polymer can be assigned with confidence.

Thermal Stability. Temperature for 5 wt % loss has often been used as a degradation temperature (T_d) to estimate thermal stability of a synthetic polymer. The T_d values for P**1** and P**2** are 355 and 342 °C, respectively (Figure 4), indicating that the polymers are thermally stable. When pyrolyzed at 800 °C, P**1** and P**2** still keep 61.4% and 41.9% of their original weights, respectively. These high weight residues should be due to thermo-cross-linking reaction of the vinyl double bonds of the (meth)acrylic pendants of the polymers at the high temperatures. This once again verifies that the monomers have been selectively polymerized by the metathesis catalyst and that the vinyl double bonds have not been cross-linked even after the monomers had been heated at 100 °C for 24 h in the polymerization reaction.

Absorption and Emission. As can be seen from Figure 5, the THF solutions of the monomers do not absorb in the spectral region beyond 330 nm. The polymers, however, absorb in the longer wavelength region, with two peaks at around 370 and 414 nm. Comparison of the absorption spectra of the polymers with those of their monomers reveals that the absorptions of the polymers in the spectral region beyond 330 nm are associated with the electronic transitions of their poly(diphenylacetylene) skeletons. The absorption characteristics of the films of the polymers are similar to those of their solutions.

Upon photoexcitation, dilute solutions of P**1** and P**2** emit green light, with emission maxima at 528 and 500 nm and Φ_F values of 41% and 47%, respectively (Figure 6A). The emission spectrum of P**1** is very broad, with a full width at half-maximum (fwhm) as wide as 118.5 nm. The spectrum of P**2** is similarly broad and seems to consist of two components, as suggested by the peak at 500 nm and the shoulder at 528 nm. The emission spectra of the thin films of the polymers appear to be red-shifted from those of their dilute solutions. Closer inspection reveals that the red shifts are actually due to the decreased contributions of the "bluer" components to the emission spectra, which narrows the spectra and decreases their fwhm's.

Comparison of the spectra of the solutions and the films suggests that the peaks in the shorter and longer wavelengths are associated with the emissions of the "monomeric" and "excimeric" species of the polymers, respectively. Excimer emission is known to be concentration dependent, and we thus studied how the concentration of P**2** solution would affect its emission spectrum. As can be seen from Figure 6B, when its concentration is increased, fwhm of its emission spectrum is quickly decreased in a linear fashion in the high concentration region.

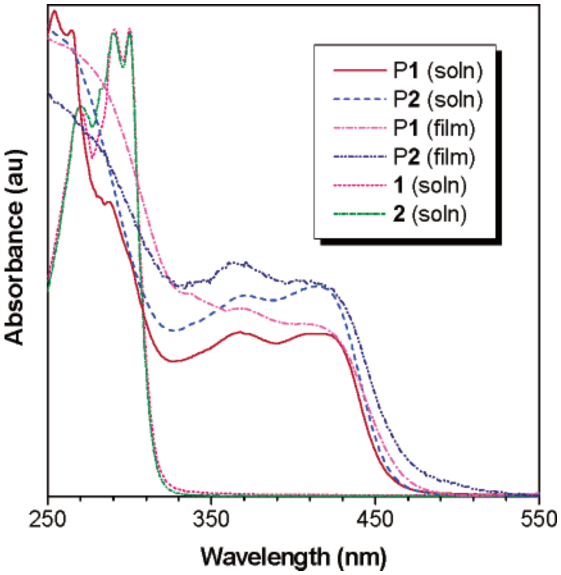


Figure 5. Absorption spectra of the THF solutions of monomers **1** and **2** and polymers P**1** and P**2** (1.56 × 10^{-4} M) and the thin films of P**1** and P**2** prepared by spin-coating their 1,2-dichloroethane solutions (2 mg/mL) onto quartz substrates.

Molecules and polymers whose phenyl groups are spatially separated by three carbon atoms, such as 1,3-diphenylpropane and polystyrene, have been found to readily form intramolecular excimers, which emit in the redder spectral region, in comparison to their "normal" monomer emissions.[24] This is the so-called "$n = 3$ rule" for the formation of intramolecular excimers (Chart 2). Theoretically, a polyene chain can take four different kinds of conformations—trans—transoid (or *E*-*s*-*E*), trans—cisoid (or *E*-*s*-*Z*), cis—cisoid (or *Z*-*s*-*Z*), and cis—transoid (or *Z*-*s*-*E*)—among which the trans—transoid conformation meets the $n = 3$ rule. The chain segments with this conformation in P**1** and P**2** form intramolecular excimers, which emit in the longer spectral region. This explains why the emission spectra of the solutions of the polymers are so broad even at a concentration as low as 3.8 × 10^{-9} M.

With an increase in the solution concentration, the probability for the phenyl pendants of the polymer chains to interact electronically will be increased, and the transannular resonance effect between the aromatic rings will be enhanced. This may help coplanarize the phenyl rings in the chain segments with trans—cisoid, cis—transoid, and cis—cisoid conformations, favoring the formation of intramolecular excimers, although here $n = 4$ for the trans—cisoid and cis—transoid conformers and $n = 6$ for the cis—cisoid conformer. Another noticeable feature is that the phenyl rings in the trans—cisoid and cis—transoid excimers are cross-"coupled" due to the involved geometric constraint, whose resonance effect will thus be smaller than that in the trans—transoid, conventional "$n = 3$" excimer. Nevertheless, the formation of the excimeric species depopulates the monomeric species. The increased contribution from the excimer emission, plus the involved energy transfer from the monomers to the excimers, shifts the emission spectrum of the polymer to the redder spectral region and narrows its fwhm.

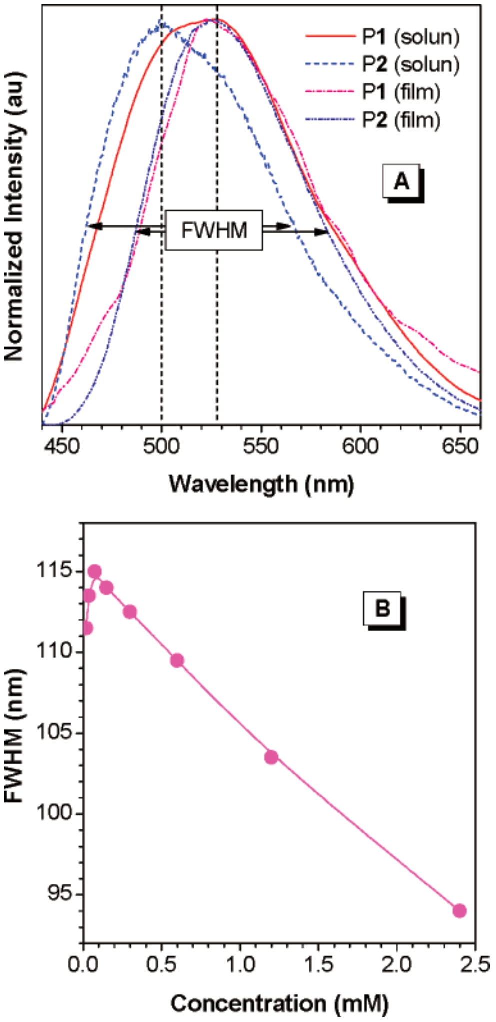


Figure 6. (A) Emission spectra of THF solutions of P**1** and P**2** (2.4×10^{-5} M) and their thin films prepared by spin-coating their 1,2-dichloroethane solutions (2 mg/mL) onto quartz substrates. Excitation wavelength: 424 nm. (B) Change in the full width at half-maximum (fwhm) of emission spectrum of P**2** with concentration of its THF solution.

Aggregation often causes spectral changes similar to those induced by concentration effect in many dye systems. To see whether this would be the case in our polymer system, we added water, a nonsolvent of P**2**, into its THF solution, which would cause the polymer chains to aggregate. As can be seen from Figure 7A, with progressive addition of water into the THF solution of P**2**, the emission spectrum of the polymer and its fwhm gradually red-shifts and narrows, respectively, similar to the effects observed in the solution thickening experiments discussed above. While aggregation normally quenches light emission, the emission of P**2** is intensified, instead of being weakened, by the aggregate formation. Its Φ_F value generally increases with increasing water fraction in the solvent mixture or with increasing extent of aggregation (Figure 7B).

Similar results are obtained in the system of P**1**: its Φ_F value increased from 41% in pure THF to 53% in a THF/water mixture with a water fraction of 90 vol %. This "abnormal" phenomenon of aggregation-enhanced emission (AEE) has also been observed in other substituted, especially disubstituted, PA systems: for example, the Φ_F value of poly(1-phenyl-1-octyne) increased by ~2.5 fold when its solvent changed from pure THF to a THF/water mixture containing 90% water.[25]

The increase in the Φ_F value of P**2** with the water content appears to be a two-step process: in the mixture with "low" water fraction (<70 vol %), Φ_F increases steadily, while in the mixture with "high" water fraction (>70%), Φ_F increases swiftly. Such a two-step process has been observed in many of our previously studied small molecule systems, especially the tetraphenylethene (TPE; $Ph_2C{=}CPh_2$) system, that exhibit the novel AEE as well as AIE (aggregation-induced emission) effects.[26] The repeat unit of P**2** may be viewed as a structural conger of TPE. The AEE effect of P**2** thus may be caused by a mechanism similar to that of TPE: the restriction of the intramolecular rotations by the aggregate formation.

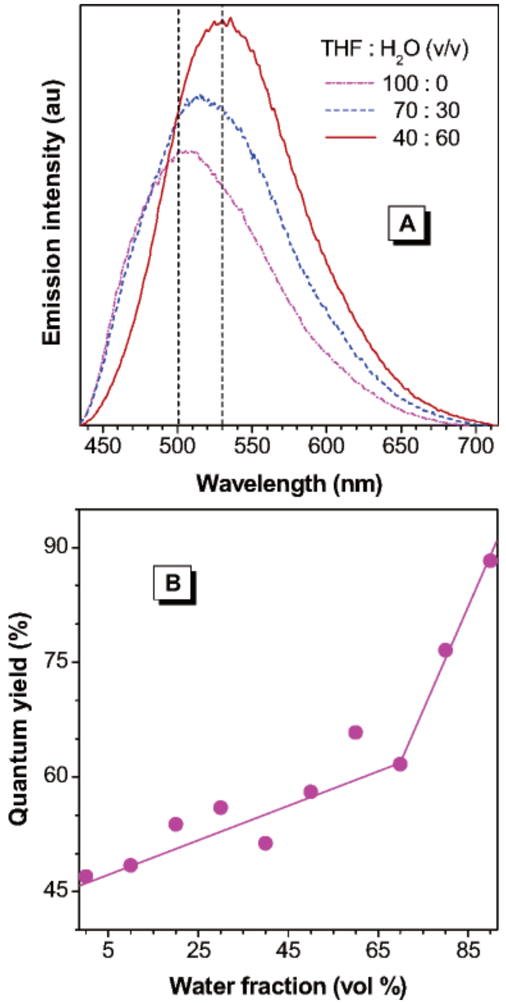


Figure 7. (A) Emission spectra of P**2** in THF/water mixtures and (B) variation in the quantum yield of fluorescence of P**2** with water content in the THF/water mixture. Polymer concentration: 2.4×10^{-5} M; excitation wavelength: 424 nm.

In the first step, the mixtures with "low" water contents are still relatively "good" solvents for the polymer chains, in which only are some segments of the polymer chains aggregated. The aggregate formation restricts the rotations of the phenyl rings against the polyene backbone, which effectively rigidifies the polymer structure, hence making the polymer more emissive. In the second step, the mixtures with "high" water fractions are relatively "poor" solvents for the polymer chains, in which the polymer chains aggregate into clusters. (The clusters should be nanosized because their suspensions are still macroscopically homogeneous and visually transparent.) In such a solvent mixture, a small increase in the water fraction will greatly populate the nanoclusters, hence the observed expeditious increase in the quantum yield.

Fluorescent Photopatterning. The luminescent imaging soft photolithography technique has potential applications in photonic

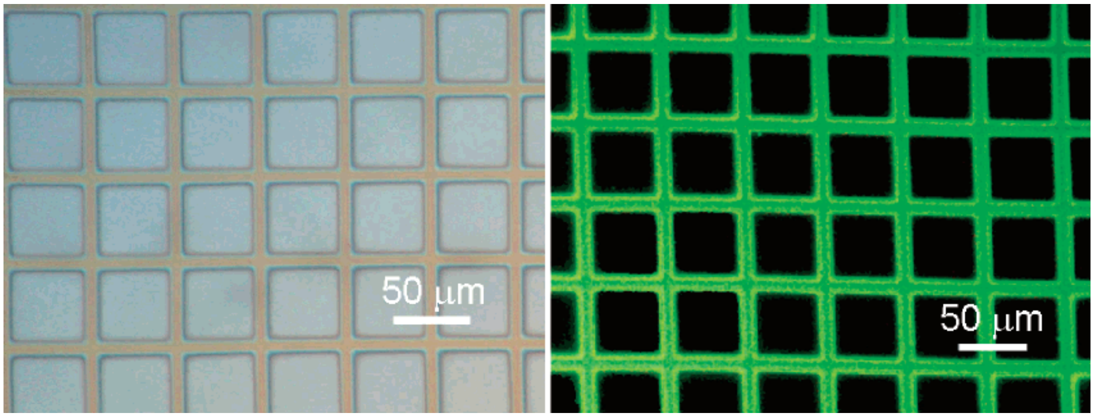


Figure 8. Negative photoresist patterns generated by photo-cross-linking of P**2**; images taken under optical (left) and fluorescent (right) microscopes.

and electronic devices and biological sensing and probing chips.[27] Using a multiple beam interference holographic lithography process, photonic crystals have been fabricated from organic polymers containing photosusceptible moieties.[28] Fluorescent conjugated polymers with photo-cross-linkability and thin-film formability are promising candidate materials for the construction of high-performance photonic devices.[29] The polymers are expected to form light-emitting patterns in pure films without phase separation upon photoirradiation.[27,30]

Upon exposure to UV light for 3 min, the (meth)acrylic groups of P**1** and P**2** are photopolymerized. The parts of their thin films uncovered by the photomasks are cross-linked, whereas the covered parts remain unchanged. After development by 1,2-dichloroethane, three-dimensional negative photoresist patterns are obtained. A set of typical photoresist images generated by the photo-cross-linking of a P**2** film is shown in Figure 8 as an example. Under an optical microscope, it is seen that the grids are regularly arranged and lines are clearly edged. Under a fluorescent microscope, the photo-cross-linked patterns emit strong green light. The photocuring ability of P**1** and P**2** offers the patterns with high thermal stability and strong solvent resistance. After development by a solvent with a high solvating power (1,2-dichloroethane), the films still retain the original patterns and sizes without any signs of swelling. After all the treatments, the films remain to be highly fluorescent upon photoexcitation.

Concluding Remarks

In summary, in this work, we have polymerized diphenylacetylene derivatives containing reactive vinyl groups and polar ester functionality (**1** and **2**). The WCl_6-Ph_4Sn mixture can selectively catalyze the metathesis polymerization of the acetylenic triple bonds and leave the vinyl double bonds unharmed. Considering that the formation of ester group via the condensation of hydroxyl and carboxylic groups is one of the most versatile organic reactions, it is anticipated that various disubstituted PA derivatives carrying functional pendants will be readily prepared using the synthetic route developed in this study.

The solutions and films of the functionalized disubstituted PAs (P**1** and P**2**) emit efficient green light upon photoexcitation. The emission spectra of the polymers shift to red and narrow in fwhm with an increase in their solution concentrations, due to the increased contributions of the emissions from the intramolecular excimeric species in the concentrated solutions. A unique yet useful AEE phenomenon is observed in the light emission processes of the polymers in the THF/water mixtures, owing to the restriction of the intramolecular rotations by the aggregate formation. The photopolymerizability of the (meth)acrylic pendants of the polymers allows their films to be patterned into fluorescent images. The cross-linked networks in the photoresists offer the patterned films with high mechanical strength, thermal stability, and etching resistance. These advantages may enable the polymers to find potential applications in the construction of polymer photonic crystals, light-emitting diodes, and backlights in liquid-crystal displays.

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