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Synthesis, light emission, and photo-cross-linking of luminescent polyacetylenes containing acrylic pendant groups

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Abstract

New poly(1-phenyl-1-alkyne)s bearing acrylic pendants (–{(C_6H_5)C=C[(CH_2)$_m$OCOCH=CH_2]}$_n$–; P**1**(m), $m=3$, 9) with high molecular weights are synthesized in high yields by WCl_6–Ph_4Sn catalyst. The structures and properties of P**1**(m) are characterized and evaluated by IR, NMR, TGA, UV, and PL analyses. All the polymers are solution-processable and thermally stable ($T_d \geq 380$ °C). Upon photoexcitation, the polymers emit strong blue lights with emission efficiencies (>40%) comparable to that of poly(1-phenyl-1-octyne), an emissive disubstituted polyacetylene. No excimeric absorption and emission are observed in the thin films of the polymers. The acrylic moieties of P**1**(m) are readily cross-linked by UV irradiation without harming their optical properties, which may enable them to find high-tech applications in photoresist, luminescent patterning, and light-emitting diodes.

Keywords: Light emission; Photo-cross-linking; Polyacetylenes

1. Introduction

Conjugated polymers have attracted considerable interest over the past decades owing to their potential applications in optics and electronics [1–5]. Thanks to the research efforts of scientists and engineers in the area, some polymers have attained electroluminescence performances up to the levels needed for real-world device applications. An efficient light-emitting diode (LED) generally consists of two or more different layers [6] to improve the injection and transportation of holes and electrons. However, in the layer-by-layer spin-coating process, the previous layer is partially dissolved by the subsequent layer to be coated, leading to lower device performance. Cross-linking the coated material before applying the next layer helps avoid redissolution [7] and hence improve the device efficiency. Conjugated polymers capable of curing, especially photo-cross-linking, have been used in manifold ways in the construction of LEDs [8–18].

Polyacetylene is the best-known conjugated polymer and shows metallic conductivity upon doping. It has, however, been generally regarded as unpromising material for LED applications because it emits weakly in the infrared region. In this work, we take a molecular engineering approach and synthesized two new 1-phenyl-1-alkynes containing acrylic moiety with different spacer lengths [**1**(m); Scheme 1]. Selective acetylene polymerizations of the monomers without harming their vinyl moieties are achieved by WCl_6–Ph_4Sn catalyst, giving completely soluble, high molecular weight polymers in high yields. The polymers are efficient blue light emitters and their acrylic pendants can be readily cross-linked by UV irradiation, generating well-defined luminescent photoresist patterns.

2. Experimental section

2.1. Materials

All the chemicals were purchased from Aldrich and used as received without further purification. 1-Phenyl-1-alkyn-($m+2$)-ols were prepared by coupling reaction of iodobenzene with

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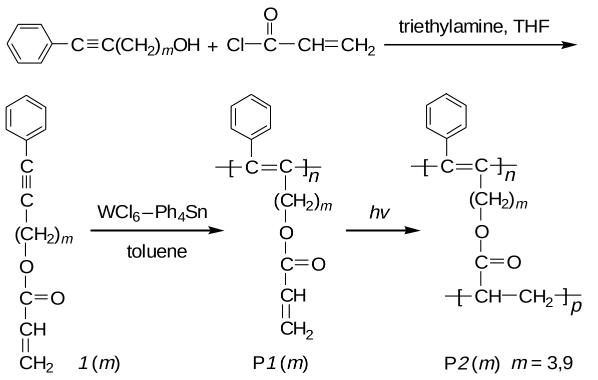

Scheme 1. Synthesis of 1-phenyl-1-alkynes containing acrylic functional groups **1**(*m*), polymerization of monomers **1**(*m*) to polymers P**1**(*m*), and photo-cross-linking of P**1**(*m*) to P**2**(*m*).

1-alkyn-($m+2$)-ols, using our previously published procedures [19].

2.2. Instrumentation

IR spectra were measured on a Perkin–Elmer 16 PC FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS) as internal reference ($\delta=0$). UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectra were measured on Perkin–Elmer LS 55 Luminescence spectrofluorometer. Mass spectra were recorded on a Finnigan TSQ 7000 triple-quadrupole mass spectrometer operating in a chemical ionization (CI) mode with methane as carrier gas. Molecular weight and polydispersity (M_w/M_n) of the polymers were estimated in THF by a Waters Associated gel permeation chromatograph (GPC) system, using polystyrene standards for molecular weight calibration. Thermal stability of the polymers was evaluated on a Perkin–Elmer TGA 7 under dry nitrogen at a heating rate of 10 °C/min.

2.3. Monomer synthesis

Monomers **1**(*m*) were prepared by reaction of acryloyl chloride with 1-phenyl-1-alkyn-($m+2$)-ols. In a 100 mL two-necked, round-bottom flask were added 0.67 g (7.5 mmoL) of acryloyl chloride and 40 mL of dry THF. The flask was cooled using an ice both. A solution of 1-phenyl-1-pentyn-5-ol (0.8 g, 5 mmoL) and triethylamine (1 mL) in 10 mL of THF was injected. The mixture was slowly warmed to room temperature and stirred overnight. THF was distilled off using a rotary evaporator. The crude product was dissolved in chloroform and washed with water twice. Purification by a silica gel column using a hexane/ethyl acetate mixture (5:1 v/v) as eluent gave monomer **1**(3) in 63.4% (0.68 g) yield. Monomer **1**(9) was prepared in a similar fashion.

Characterization: **1**(3): colorless liquid; yield 63.4%. IR (KBr), ν (cm^{-1}): 2930, 2856, 2202 (C≡C), 1724 (C=O), 1636 (C=C), 1618, 1596, 1490, 1407, 1271, 1192, 810, 756, 691. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.69, 7.24 (m, 5H, Ar–H), 6.44, 6.13, 5.83 (m, 3H, CH=CH$_2$), 4.32 (t, 2H, CO$_2$CH$_2$), 2.53 (t, 2H, ≡CCH$_2$), 2.02 (t, 2H, ≡CCH$_2$C*H*$_2$). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 166.1, 131.5, 130.7 (=*C*CO$_2$), 128.4 (=CH$_2$), 128.1, 127.6, 123.6, 88.5 (≡*C*CH$_2$), 81.2 (Ar*C*≡), 63.2, 27.8, 16.2. MS (CI): *m/z* 215.1 $(M+1)^+$.

1(9): colorless liquid; yield 81.3%. IR (KBr), ν (cm^{-1}): 2929, 2857, 2205 (C≡C), 1725 (C=O), 1636 (C=C), 1618, 1597, 1490, 1407, 1271, 1192, 811, 756, 692. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.40, 7.24 (m, 5H, Ar–H), 6.44, 6.12, 5.82 (m, 3H, CH=CH$_2$), 4.15 (t, 2H, CO$_2$CH$_2$), 2.39 (t, 2H, ≡CCH$_2$), 1.64 [m, 4H, ≡CCH$_2$(C*H*$_2$)$_2$], 1.47–1.33 [m, 10H, (CH$_2$)$_5$]. ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 166.3, 131.5, 130.4 (=*C*CO$_2$), 128.6 (=CH$_2$), 128.1, 127.4, 124.1, 90.4 (≡*C*CH$_2$), 80.6 (Ar*C*≡), 64.7, 29.4, 29.2, 29.0, 28.8, 28.7, 28.6, 25.9, 19.4. MS (CI): *m/z* 299.2 $(M+1)^+$.

2.4. Polymerization

All the polymerization reactions and manipulations were carried out under nitrogen using an inert-atmosphere glove box. Typical experimental procedures for the polymerization of **1**(3) are given below: Into a baked 20 mL Schlenk tube with a stopcock in the sidearm was added 172 mg (0.8 mmol) of **1**(3). The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the side arm. 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 the monomer solution was transferred to the catalyst solution using a hypodermic syringe. After stirring at 60 °C for 24 h, the solution was cooled to room temperature, diluted with 10 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: P**1**(3): pale yellow solid; yield 76.2%. M_w 51 700; M_w/M_n 2.3 (GPC; Table 1, No. 2). IR (KBr), ν (cm^{-1}): 3053, 2958, 2894, 1723 (C=O), 1636 (C=C), 1619, 1598,

Table 1
Polymerization of **1**(3) and **1**(9)

No.	Temp[a] (°C)	Yield (%)	M_w[b]	M_w/M_n[b]
		Monomer **1**(3)		
1	rt	Trace		
2	60	76.2	51,700	2.3
3	80	47.5	23,600	1.8
		Monomer **1**(9)		
4	rt	Trace		
5	60	72.1	55,300	2.3
6	80	45.4	25,700	1.7

Catalyzed by WCl$_6$–Ph$_4$Sn in toluene under nitrogen for 24 h; $[M]_0=0.2$ M, [cat.] = [cocat.] = 10 mM.

[a] Abbreviation: rt, room temperature.

[b] Estimated by GPC in THF on the basis of a polystyrene calibration.

1490, 1442, 1408, 1296, 1272, 1191, 1056, 985, 810, 763, 698. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.99 (Ar–H), 6.29, 6.08, 5.78 ($CH{=}CH_2$), 3.79 (OCH_2), 1.88 (OCH_2CH_2), 1.74 (CH_2). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 166.1, 139.9 (PhC=*C*), 130.9 (=*C*CO_2), 128.5 (=CH_2), 64.6, 30.3, 15.3.

P**1**(9): pale yellow solid; yield 72.1%. M_w 26 800; M_w/M_n 1.68 (GPC; Table 1, No. 5). IR (KBr), ν (cm^{-1}): 3051, 2955, 2896, 1724 (C=O), 1636 (C=C), 1619, 1598, 1491, 1441, 1408, 1296, 1271, 1190, 1056, 985, 810, 764, 699. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.91 (Ar–H), 6.36, 6.12, 5.81 ($CH{=}CH_2$), 4.13 (OCH_2), 2.40 (OCH_2CH_2), 1.62–1.26 $(CH_2)_7$. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 166.2, 142.8 (PhC=*C*), 130.4 (=*C*CO_2), 128.6 (=CH_2), 127.0, 64.6, 35.7, 29.4, 28.6, 26.0, 19.4.

2.5. Photopolymerization and photopatterning

Photo-cross-linking of the polymer films were conducted using the 365 nm light obtained from a Spectroline ENF-280C/F UV lamp in vacuum. The incident light intensity was ~32 mW/cm^2. The polymer films were prepared by spin-coating the polymer solutions (~2 wt % in 1,2-dichloroethane) at 2000 rpm for 1 min on quartz plates. The thickness was ~1.2 μm. The films were dried in vacuum at 40 °C for 3 h. 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. The weights of the films were measured by a Perkin–Elmer AD-6 Autobalance with accuracy of ±0.01 mg. The weight percentage of the insoluble fraction was then plotted against irradiation time.

The photoresist patterns were prepared on silicon wafer using a Cu-negative mask. The polymer solutions were coated and the resultant thin films were baked following the standard procedures for photosensitivity study. After UV irradiation, the films were developed in 1,2-dichloroethane for 2 min. The films were heated at 80 °C for 2 h and the fluorescent images were taken on a fluorescent optical microscope (Olympus BX41).

3. Results and discussion

3.1. Monomer preparation

With a view of synthesizing light-emitting polyacetylenes with photo-cross-linkable pendant groups, we designed the molecular structures of two 1-phenyl-1-alkynes containing acrylic functionalities with different lengths of spacer. The monomers were synthesized according to Scheme 1 and isolated in high yields. They were characterized by standard spectroscopic methods, from which satisfactory analysis data corresponding to their molecular structures were obtained (Section 2).

3.2. Polymer synthesis

Since WCl_6–Ph_4Sn is an effective catalyst for the polymerizations of 1-phenyl-1-alkynes [19], we tried to polymerize **1**(*m*) using this binary mixture. Reaction of **1**(3) catalyzed by WCl_6–Ph_4Sn in toluene at room temperature, disappointedly, gives only a trace amount of polymeric product (Table 1, No. 1). Gratefully, a high molecular weight polymer is isolated in a high yield when the polymerization is conducted at 60 °C. Further increment of the temperature to 80 °C, however, lowers the polymer yield, probably due to the instability of the catalytic species and/or activation of termination reactions at high temperatures. The polymerization behaviors of **1**(9) are similar to those of **1**(3). While almost no polymers are obtained at room temperature, polymerizations conducted at elevated temperatures produce polymers with molecular weights up to 5.5×10^5 in high yields (Table 1, Nos. 5 and 6).

3.3. Structural characterization

All the polymers are completely soluble in common organic solvents such as chloroform, THF and toluene and are thermally very stable with onset degradation temperatures (T_d) of ≥380 °C. The high thermal stability of the polymers may be related to the 'jacket effect' of the phenyl groups [19–22], which wrap the polyene backbones and thus limit their perturbation by heat and/or shield them from the attack by degradative species such as oxygen. The acrylic pendant groups may undergo thermal polymerization at high temperatures. The resulting polyethylene chains may provide additional protection to the labile polyacetylene backbones against the thermolytic decomposition.

The molecular structures of the polymers are confirmed by IR and NMR spectroscopic analyses. Examples of ^{13}C NMR spectra of P**1**(9) and its monomer **1**(9) are given in Fig. 1. The acetylenic and vinyl carbon atoms of **1**(9) absorb at δ 90.4 and

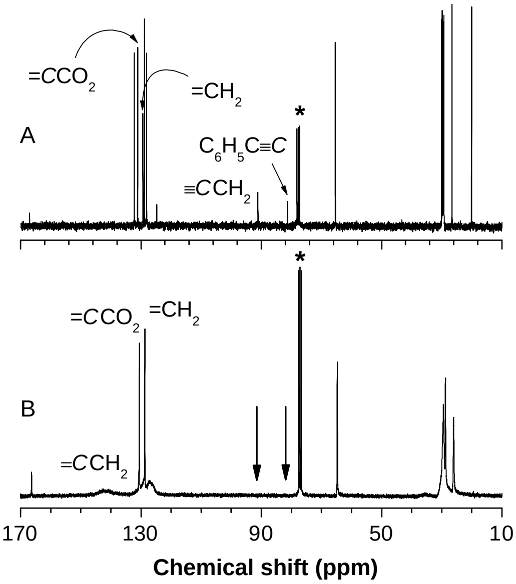

Fig. 1. ^{13}C NMR spectra of (A) **1**(9) and (B) its polymer P**1**(9) (sample taken from Table 1, No. 5) in chloroform-*d*. The solvent peaks are marked with asterisks (*).

80.6, and 130.4 and 128.6, respectively. While the first two peaks disappear after polymerization, the latter two peaks are still observed in the spectrum of **P1**(9). A new broad peak associated with the absorption of the polyene carbon is found at δ 142.9, indicating that the catalyst has selectively polymerized the acetylene unit of **1**(9), while leaving the acrylic functionality intact.

3.4. Absorption and emission

The UV and PL spectra of **P1**(3) and **P1**(9) in THF and solid thin films are given in Fig. 2. Since monomer **1**(3) does not absorb photons at wavelengths longer than 300 nm, the absorptions at the longer wavelength regions of **P1**(3) in THF are thus obviously from the double-bond polyene backbones (Fig. 2(A)). The ground-state electronic transitions of the polymers are affected little by the spacer length: the UV spectrum of **P1**(9) is similar to that of **P1**(3) with slightly higher absorptivity.

The polymers are strong blue light emitters. Upon UV excitation, their poly(1-phenyl-1-alkyne) backbones emit strong blue light of 460 nm in THF. The quantum yields (Φ_F) calculated for **P1**(3) and **P1**(9), using 9,10-diphenylanthracene as reference ($\Phi_F = 90\%$ in cyclohexane) [23], are 44 and 47%, respectively, which are similar to that of poly(1-phenyl-1-octyne) (PPO) [24–26], a well-known highly luminescent disubstituted polyacetylene.

Many conjugated polymers emit intensely in solutions but become weakly luminescent when fabricated into films [27–30]. This is mainly caused by strong interchain interaction in the solid state. The UV and PL spectra of **P1**(3) and **P1**(9) films are, however, almost identical to those of their solutions (Fig. 2(B)), suggestive of little or no excimeric absorption and emission. The long alkyl chains of the polymers may have hampered the stacking of the polyacetylene chains, thus

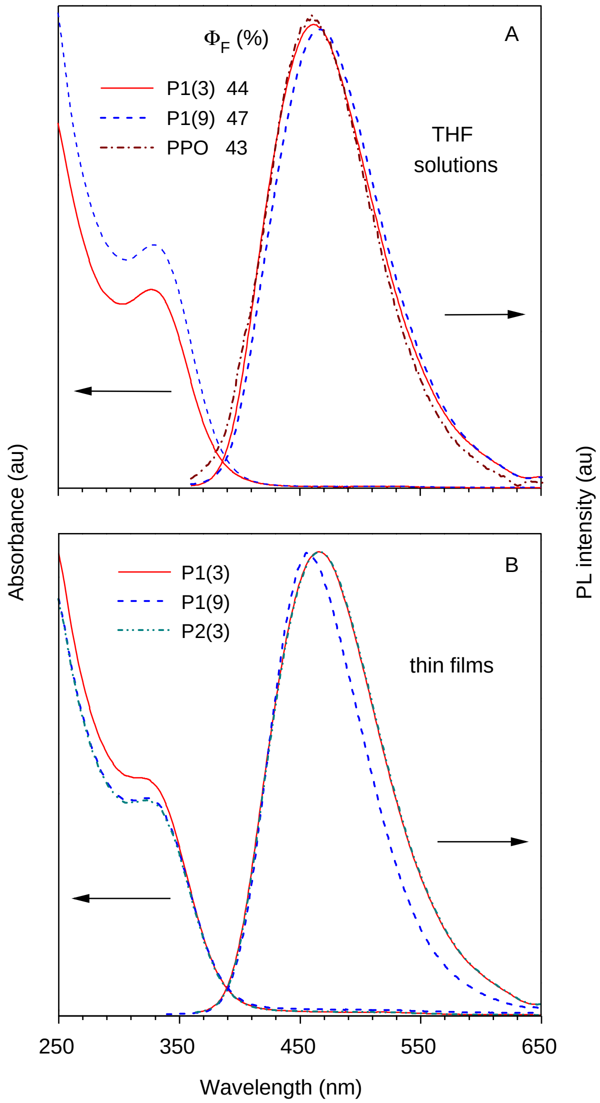

Fig. 2. Absorption and emission spectra of **P1**(3), **P1**(9) (samples taken from Table 1, Nos. 2 and 5), **P2**(3), and PPO in (A) THF solutions and (B) solid thin films. Solution concentration: 0.0025 mg/mL; excitation wavelength: 330 nm.

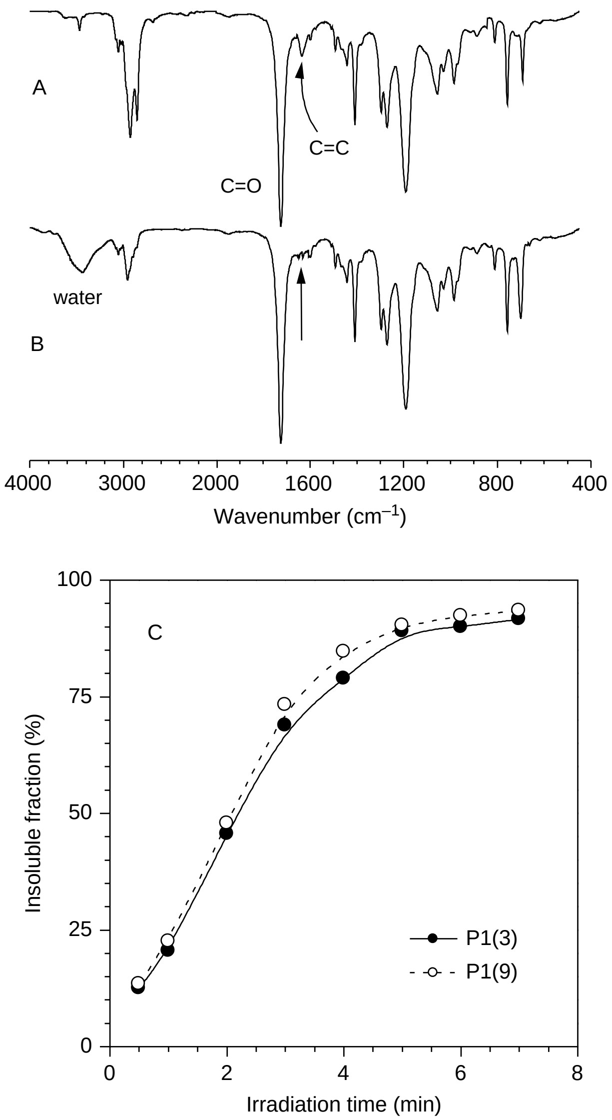

Fig. 3. IR spectra of (A) **P1**(9) (sample from Table 1, No. 5) and (B) **P2**(9), and (C) plots of insoluble fractions of thin films of **P1**(3) (Table 1, No. 2) and **P1**(9) versus irradiation time.

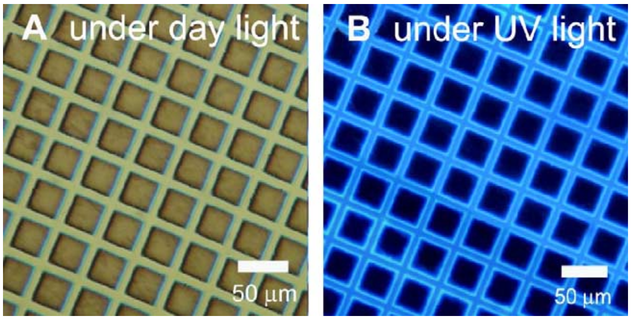

Fig. 4. Three-dimensional negative photoresist images generated by photo-cross-linking of P**1**(3) (sample from Table 1, No. 2) taken under (A) normal laboratory light and (B) a handheld UV lamp. Scale bar: 50 μm.

enabling P**1**(3) and P**1**(9) to emit efficiently even when fabricated into thin films. We tried to measure their Φ_F values but no reliable data could be obtained.

3.5. Photopolymerization and photopatterning

The polymers can be cast into tough films by spin-coating their solutions. To investigate whether the acrylic pendants can be photopolymerized, we irradiated the polymer films in Schlenk tubes under vacuum by a UV lamp with a power of ~ 32 mW/cm^2. The changes in the films are monitored by IR spectroscopy. The absorption peak associated with C=C stretching vibration at ~ 1637 cm^{-1} becomes weaker progressively with time, which is consistent to the polymerization of carbon–carbon double bonds (Fig. 3). The insoluble fraction of the polymer film increases exponentially with time and reaches $>90\%$ in 7 min, irrespective of the spacer length (Fig. 3(C)). We measured UV and PL spectra of the cross-linked polymers P**2**(*m*) [Fig. 2(B) for P**2**(3) as an example] and found that they were similar to those of P**1**(*m*), proving the irradiation resistance of the films during the photo-cross-linking reaction.

Since P**1**(3) and P**1**(9) are photoresponsive, we explored the possibility of utilizing them to fabricate luminescent patterns. UV irradiation of P**1**(3) readily initiates photopolymerization of its acrylic pendants. Development of the exposed films [31] gives a well-defined photoresist pattern (Fig. 4(A)). The patterned lines glow under UV illumination (Fig. 4(B)) because the poly(1-phenyl-1-alkyne) skeleton of P**1**(3) is highly emissive.

4. Conclusion

In this work, we successfully synthesized two new poly(1-phenyl-1-alkyne)s containing acrylic functional pendants and studied their light-emitting and photo-cross-linking properties. Polymers of high molecular weights are prepared in high yields by WCl_6–Ph_4Sn catalyst. The polymers are film forming and thermally stable. Upon photoexcitation, they emit strong blue light of 460 nm in both solution and solid states. The acrylic pendants can be readily polymerized by UV irradiation, generating well-defined luminescent photoresist patterns. The polymers may find technological applications in photonic and electronic systems.

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